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"Nec aranearum sane textus ideo melior quia ex se fila gignunt, nec noster vilior quia ex alienis libamus ut apes." Just. Lips. *Polit.* lib. i. cap. 1. Not.

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"Meditationis est perscrutari occulta ; contemplationis est admirari perspicua . . . . Admiratio generat quæstionem, quæstio investigationem, investigatio inventionem."—*Hugo de S. Victore.*

———

——"Cur spirent venti, cur terra dehiscat,
Cur mare turgescat, pelago cur tantus amaror,
Cur caput obscura Phœbus ferrugine condat,
Quid toties diros cogat flagrare cometas,
Quid pariat nubes, veniant cur fulmina cœlo,
Quo micet igne Iris, superos quis conciat orbes
Tam vario motu."

J. B. Pinelli ad Mazonium.

ALERE FLAMMAM.
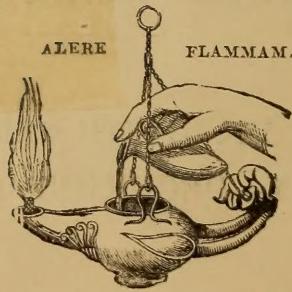
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PLATES.

I. *The Fundamental Atomic Laws of Thermochemistry.* *By* WILLIAM SUTHERLAND [*].

THE data of Thermochemistry have been made the subject of many general suggestions as to relations and laws holding amongst them, but these suggestions have for the most part remained undeveloped and uncoordinated. It is true that Thomsen and Berthelot, to whom we owe the greater part of the splendid accumulation of experimental material, have ever had in view the deduction of generalizations from their data wherewith to enrich chemical philosophy on the side of energetics : thus Berthelot discovered his principle of maximum heat ; and Thomsen marshalled the facts of the thermochemistry of carbon compounds into an orderliness in which he was able to show the operation of some beautifully simple principles. Unfortunately a few invalid assumptions and speculations introduced by Thomsen into his theoretical systemization of carbon thermochemistry seem to have made many chemists afraid that they have involved his whole system in their invalidity. But in reality these assumptions are quite unnecessary, and when banished from Thomsen's system leave his discoveries a grand unobstructed main road into the region of thermochemical law. Thomsen's generalizations relate to the carbon compounds

only, although by his experiments he also put upon a satisfactory footing the only general principle that has yet been discovered in organic thermochemistry; namely, the principle practically enunciated in different forms by Hess, Andrews, and Favre and Silbermann, that in the formation of salts in solution from their elements each atom contributes an amount of heat which is approximately independent of the other atoms with which it is associated. More recently Tommasi (*Comptes Rendus*) and others have occupied themselves with this law, which indeed has for some little time been installed in text-books as the one generalization of value that the thermal branch of chemistry has yet contributed to the science. Quite recently Dieffenbach (Abst. Journ. Chem. Soc. 1890, p. 1206) has tried to show that also in entering into the molecule of an organic compound, an atom of an element always produces the same amount of heat; and there is no doubt that this has been a fair enough hypothesis with which to investigate the accumulating store of experimental material, but it will be made manifest in this paper that this hypothesis must be abandoned in favour of one which provides for a dependence of the atoms on one another in the matter of heats of combination.

The present paper embodies an attempt to unfold the fundamental atomic thermochemical laws in operation both amongst inorganic and organic compounds. In the First Part, after an introductory chapter, the laws regulating the thermochemistry of the haloid compounds of the metals are developed; and in the Second Part Thomsen's theoretical systemization of carbon thermochemistry will be gone over step by step with a view to eliminating a few principles that seem untenable, and to re-stating his discoveries in terms harmonious with the principles which will be shown to rule the greater part of thermochemistry.

One of the chief conditions which contributed to Thomsen's success in the handling of the data of the thermochemistry of the carbon compounds, was that he studied the heat of formation of the compounds in the gaseous state. The ideal condition in which the data of thermochemistry should be presented is that in which they relate to the heat of formation at constant volume of the gaseous product from gaseous elements; for these would be the pure heats of formation of the compound molecule from the elementary, unmixed with latent heats or heat spent in external work. In the thermochemistry of the carbon compounds the latent heat of vaporization of carbon is unknown, so that Thomsen was not able to put his data actually into the ideal condition, although he

lid so as nearly as he could. But considerable progress can be made in the thermochemistry of carbon compounds without a knowledge of the heat of vaporization of carbon ; for many different types of compound involving the same number of carbon atoms in their molecules can be studied, and in the differences of their heats of formation the unknown quantity disappears. Still, in striving for more comprehensive results, Thomsen made certain assumptions in order to obtain, as a single known quantity, the unknown latent heat of the carbon molecule plus its heat of formation from atoms. These have been a stumbling-block to many chemists on account of their arbitrary nature ; and although Thomsen seems to have abandoned them and the value of the latent heat plus heat of formation of the gramme-molecule of carbon as unsound, a certain distrust of even his sound conclusions still lingers. In the second part of this paper Thomsen's analysis of the thermochemical data of carbon compounds will be restated in a brief form, with removal of the few unwarranted and unnecessary parts.

But in the thermochemical data of inorganic compounds, which will be studied in the first part of the paper, the cause of the little progress that has been made in the discovery of general principles amongst them is the fact that it has not been possible to get them into the ideal state—that is, referred to the gaseous condition of both the agents and the products. Of course for a certain number of inorganic compounds the data can be obtained for the gaseous state, but these have been too few to give a clue to any general thermochemical law ; and the data for the compounds of most of the metals hitherto available are not pure thermochemical data at all, but contain, as it were, unknown amounts of impurity in the shape of unknown latent heats. It is obvious, therefore, that the pure thermochemical laws cannot be discovered until these latent heats are known : that is, for instance, until the heat of combination of gaseous Na with gaseous Cl to produce gaseous NaCl is known. Notwithstanding recent progress in chemical manipulation at high temperatures and the promising possibilities of the electric furnace, it may be some time yet before actual experimental values of the latent heat of vaporization of a metal like copper, or of a compound like sodium chloride are available. But in the course of a series of researches on molecular force and of another research on a kinetic theory of solids, I have been led to results which enable approximate values of the latent heat of vaporization of the metals and their compounds to be calculated. The details of the reasoning by which the methods of calculation

are established can be followed in my different papers on Molecular Force and on a Kinetic Theory of Solids in the Philosophical Magazine; but for the convenience of chemical readers, I will reproduce here briefly the essential steps of the reasoning, with the formulæ necessary for thermochemical applications. This will form the Introduction to Part I., which will deal with inorganic compounds, Part II. relating to organic.

INTRODUCTION.

The starting-point in the application of Dynamics to molecular physics is the Virial equation of Clausius. If a number of molecules (forming, say, a unit mass) are confined in a volume v at pressure p, and if $\frac{1}{2}m\mathrm{V}^2$ is the kinetic energy of translatory motion of any one, and $\phi(r)$ the force acting between any two at distances r apart, then the Virial equation is

$$\tfrac{3}{2}pv = \Sigma\tfrac{1}{2}m\mathrm{V}^2 - \tfrac{1}{2}\cdot\tfrac{1}{2}\Sigma\Sigma r\phi(r) ; \quad . \quad . \quad . \quad (1)$$

where the single Σ denotes that the values of $\frac{1}{2}m\mathrm{V}^2$ for all the molecules are to be added together, while the double symbol $\Sigma\Sigma$ denotes first that all the values of $r\phi(r)$ are to be added for the forces between one particular molecule and all the rest, and then that all such sums for all particular molecules are to be added together. The best known attempt to transform this equation to a form suitable for physical applications is that which resulted in the now famous equation of van der Waals, namely,

$$pv = \mathrm{R}\theta + \mathrm{R}\theta\frac{b}{v-b} - \frac{a}{v}, \quad . \quad . \quad . \quad . \quad (2)$$

the separate terms of which are to be interpreted as follows:— θ is absolute temperature, $\mathrm{R}\theta$ stands for $\frac{2}{3}\Sigma\frac{1}{2}m\mathrm{V}^2$, and $\mathrm{R}\theta b/(v-b)$ stands for two thirds of that part of $-\frac{1}{2}\cdot\frac{1}{2}\Sigma\Sigma r\phi(r)$ which results from the forces of repulsion that act during the collisions of molecules, while $-a/v$ stands for two thirds of that part of $-\frac{1}{2}\cdot\frac{1}{2}\Sigma\Sigma r\phi(r)$ resulting from the steady attraction of the molecules which produces the cohesion of liquids and solids. The experiments of Amagat, and later of Ramsay and Young, proved that the equation of van der Waals cannot represent the facts of the vapours of compounds; and from these experiments I showed that the equation of van der Waals applies, so far as we know at present, only to the gaseous state of hydrogen, oxygen, nitrogen, and methane, and that a different form represents the main facts of most compound vapours. The point of most importance in this form for present applications is that the part of $-\frac{1}{2}\cdot\frac{1}{2}\Sigma\Sigma r\phi(r)$

resulting from the attractions of molecules for one another takes the form $-\frac{3}{2}\dfrac{l}{v+k}$, where k is nearly equal to the critical volume, and l is a constant for each substance but different for different substances (a parameter); at volume k this becomes $-\frac{3}{2}l/2k$, and for volumes below k, that is for the liquid state, the term retains the form $-\frac{3}{2}l/2v$. The constant l is thus an important measure of molecular attraction amongst like molecules, and five chief methods along with some subsidiary ones are given for calculating its value from available data, a large number of values being tabulated (Phil. Mag. 5th ser. vol. xxxv. March 1893) in the form M^2l, where M is the ordinary molecular mass (weight) of the substance. The equation of one of these methods throws light on the matter in hand; it is that of the third method,

$$Ml/v_1 = 66\cdot5\,M\lambda - 101\,T_b, \quad . \quad . \quad . \quad . \quad (3)$$

where λ is the latent heat of vaporization of a gramme of liquid at its ordinary boiling-point T_b reckoned from absolute zero, v_1 being the volume of a gramme in cubic centimetres at that temperature: with λ in calories this equation gives l in terms of 10^6 dynes as unit of force. In connexion with this equation it is shown that for a large number of liquids the approximate relation $M\lambda = 19\cdot4\,T_b$ holds; that is, the molecular latent heat is proportional to the absolute boiling-point, a relation discovered empirically by Pictet in 1876. Using this to eliminate T_b from our equation, we have approximately

$$Ml/v_1 = 61\cdot3\,M\lambda. \quad . \quad . \quad . \quad . \quad . \quad (4)$$

This shows how, if we can obtain values of l, we can derive the latent heat of vaporization of the substance as liquid. The latent heat of fusion of solid to liquid is for most bodies only a fraction of the heat of vaporization of the liquid; so that if in the last equation we replace v_1, the volume of the liquid at its boiling-point, by v the volume of the solid, we shall have an approximate equation for the heat of vaporization of the solid. The problem of finding the latent heat of vaporization of solids is thus reduced to that of finding values of l. The fifth method of finding l given in the Laws of Molecular Force is the only one of the five which is applicable to existing data for solids: the equation of that method is

$$l = c\alpha v^{5/3}/M^{1/3}; \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

where α is the surface-tension of the liquid measured in grammes weight per linear metre at two thirds of the absolute

critical temperature, v the volume of a gramme at that temperature, and M the molecular mass, c being a constant the same for all bodies. Now the surface-tensions of a number of solids at their melting-points, or, more accurately, of a number of liquids at their solidifying-points, were measured some time ago by Quincke (Pogg. *Ann.* cxxxv. p. 138), and quite recently by Traube (*Ber. der Deut. Chem. Ges.* xxiv. p. 3074). Quincke's data relate to a number of metals and a few salts, and Traube's to a number of salts of Na and K. It is obvious that there must be a certain amount of roughness in the measurements at the high temperatures of the melting-points of these bodies, and there is also an inaccuracy in the equation by which Quincke calculates the surface-tensions from the experimental measurements; but there is a compensating cause at work, and it may be said that both Quincke's and Traube's data give a fairly accurate estimate of the surface-tension at the melting-point, if all the difficulties of the measurements are allowed for. Now in our last equation (5) the surface-tension is supposed to be measured at two-thirds of the absolute critical temperature, though with a different value of c it might be taken at any constant fraction of the critical temperature. Melting-points are hardly likely to be proportional to critical temperatures; but still, as high melting-points on the whole mean high critical temperatures, there is a rough proportionality between melting-temperature and critical; so that if we denote the surface-tension at the melting-point by α_m, and the value of a gramme at ordinary temperatures by $1/\rho$, we can replace the last equation by the approximate form

$$l = c' \alpha_m (1/\rho)^{5/3}/M^{1/3}, \quad . \quad . \quad . \quad . \quad (6)$$

where c' is a constant to be determined. The value of c in (5) is 2×5930 when 10^6 dynes is the unit of force; for c' I have adopted the value 9300. To get values to join on naturally with those tabulated in the "Laws of Molecular Force," where the unit of force used is 10^{12} dynes, we can write our present relation in the form

$$M^2 l = 9300 \times 10^{-6} \alpha \ (M/\rho)^{5/3}. \ . \quad . \quad . \quad . \quad (7)$$

N.B.—Here and hereafter the unit of force is 10^{12} dynes.

By this equation, then, we can get approximate values of l for the metals and salts of Quincke's and Traube's experiments, and so deduce approximate values of their latent heats of vaporization; but as for thermochemical applications we require the latent heats of a larger number of substances,

we will proceed with an account of another method of obtaining more numerous values of l. This second method is founded on a Kinetic Theory of Solids (Phil. Mag. 5th ser. vol. xxxii.). The fundamental equation there established relates to a collection of equal monatomic molecules of diameter E or distance E between the centres of two molecules when they are in contact, e being the average distance apart of two adjacent molecules, so that $e-\mathrm{E}$ is the distance through which a molecule swings between an encounter on one side and an encounter on the opposite side ; with the same meaning as before for the other symbols, the equation for a solid free from external force is

$$\frac{2\Sigma\frac{1}{2}m\mathrm{V}^2}{3e^2(e-\mathrm{E})} - \frac{1}{6e^3}\Sigma\Sigma r\phi(r)=0. \quad . \quad . \quad . \quad . \quad (8)$$

This equation applies to the metals : as before, $\Sigma\Sigma r\phi(r)/6$ reduces to $l\rho$, where ρ is the density, and $e^3=m/\rho$, so that

$$\mathrm{M}^2l=\frac{2m\Sigma\frac{1}{2}m\mathrm{V}^2}{3e^2(e-\mathrm{E})}\left(\frac{\mathrm{M}}{\rho}\right)^2 \quad . \quad . \quad . \quad (9)$$

(it should be noticed that m denotes the actual mass of a molecule, M its ordinary molecular mass (weight) referred to hydrogen). Now $\Sigma\frac{1}{2}m\mathrm{V}^2$ is the kinetic energy of the oscillatory translatory motion of the molecules in unit mass, which is equal to $2\mathrm{J}c\theta$ if the internal energy of the molecules is negligible, where θ is the temperature, c the specific heat, and J the mechanical equivalent of heat, and $e^2(e-\mathrm{E})=\mathrm{E}^3(e/\mathrm{E}-1)$ approximately : if the molecules are invariable with temperature, $e/\mathrm{E}-1=b\theta$, where b is the coefficient of linear expansion of the metal. But it was shown in " A Kinetic Theory of Solids " that the metals behave as if E diminishes with rising temperature in such a way as to make $e/\mathrm{E}-1 =7b\theta$ approximately, and as $\mathrm{E}^3=m/\rho$ nearly, we have

$$\mathrm{M}^2l=\frac{2\mathrm{J}c\mathrm{M}(\mathrm{M}/\rho)}{21b} \quad . \quad . \quad . \quad . \quad . \quad (10)$$

In this cM, by Dulong and Petit's law, is nearly 6·4 for all the metals : the values of b have not been found experimentally for several of the most important metals, but can be obtained by an empirical relation given in " A New Periodic Property of the Elements " (Phil. Mag. [5] xxx. ; also xxxii. p. 540), namely, if T is the absolute melting-point, $b\mathrm{TM}^{1/6}=·044$;

with $4\cdot2 \times 10^7$ as the value of J, we get finally with 10^{12} dynes as unit of force,

$$M^2l = 5\cdot8(M/\rho)'TM^{1/6} \times 10^{-4}. \quad . \quad . \quad . \quad (11)$$

Thus l, and therefore the latent heat of vaporization of nearly all the metals can be found ; but we also require a similar equation for the compounds of the metals.

The establishment of such an equation is sketched in section 9 of " A Kinetic Theory of Solids," but in a form which is not correct without a strained interpretation of some of the symbols : the correct equation for a compound whose molecule contains n_1 atoms of mass m_1 and n_2 of mass m_2 and so on, the diameters of the atoms being E_1, E_2 and so on, and the mean distances from their neighbours (centre to centre) e_1, e_2 and so on, is

$$\Sigma \frac{1}{3e^3}\left(\frac{n_1 m_1 V_1{}^2}{1-E_1/e_1} + \frac{n_2 m_2 V_2{}^2}{1-E_2/e_2} + \ldots\right) = \frac{1}{6e^3}\Sigma\Sigma r\phi(r), . \ (12)$$

where as before e^3 is the domain of a molecule, that is, its share of the total space occupied by the solid, and $\phi(r)$ is the force between two molecules. The values of $E_1, E_2, e_1, e_2,$ and so on are unknown, but it is reasonable to suppose that for approximate purposes $1-E_1/e_1$ and so on can be replaced by a single mean value proportional to $b\theta$, where b is the linear coefficient of expansion of the solid compound : thus we replace each by $ab\theta$, corresponding to the $7b\theta$ for metals, then we have the sum $\Sigma(n_1 m_1 V_1{}^2 + n_2 m_2 V_2{}^2 + \ldots)$ of which the value is $2JMc\theta$, M being the molecular mass and c the specific heat of the compound. The only unknown quantity remaining is b, which has been found for very few compounds ; in the case of metals we eliminated it by the relation $bTM^{1/6} = \cdot044$. Let us assume that a similar relation holds for compounds, namely that $bTM^{1/6}$ is constant, then merging this constant and the unknown a into a single coefficient we finally reduce the last equation to the form

$$M^2l = 5\cdot8 \times 10^{-4}k \cdot \frac{Mc}{6\cdot4}(M/\rho)TM^{1/6}, \quad . \quad . \quad . \quad (13)$$

where k is a parameter to be determined for each type of compound. I have found that $k = \frac{1}{2}$ for such binary compounds as NaCl, KI, and so on ; and according to the principle of Joule and Kopp that the molecular specific heat of a compound is the sum of the atomic specific heats of its atoms, Mc for these binary compounds is $2 \times 6\cdot4$. Thus for compounds of this type the equation (13) simplifies down till it is

identical with (11), which was established for the metals; and I have found this same equation to hold for compounds of the types RS_2, RS_3, RS_4, such as $CaCl_2$, $AlCl_3$, and $SnCl_4$. When S instead of being an atom is a compound radical such as NO_3, the equation (13) does not become so simple, but in it we must put the value of Mc and take k as we have already implied that it is, namely the reciprocal of the number of radicals in the molecule. Thus in equation (13) a second method of finding l has been established, depending only on density and melting-point.

There is still another approximate method which comes in useful for a number of compounds which are liquid at ordinary temperatures and for which only density and boiling-point are known; it is

$$M^2l = 1190 \times 10^{-6}(M/\rho)T_b. \quad . \quad . \quad . \quad . \quad (14)$$

We have now to determine in what way we ought to pass from the values of l given by the three equations (7), (11), and (13) to the total latent heat of vaporization of the solid at ordinary temperatures, say $15°$ C. We have seen that for the latent heat of vaporization of a liquid at its ordinary boiling-point (4) holds when the unit of force is 10^6 dynes; with 10^{12} dynes as unit it becomes

$$Ml/v_1 = 61·3 \times 10^{-6}M\lambda.$$

But in thermochemical experiments we have, as a rule, to do with the heat given out when the reagents are taken at about $15°$ C., and the products are brought back to the same temperature, and in most cases the latent heat at $15°$ C. will be larger than at the boiling-point. Under these circumstances it seems to me best to regard the matter in the following way : l/v is the potential energy of the molecules of a gramme occupying volume v, due to their mutual attractions; hence if v_0 is the volume of the gramme when solid, and v_3 is a large volume into which it is supposed to be vaporized, the change of potential energy, due to the separation of the molecules in a gramme-molecule, is $Ml/v_0 - Ml/v_3$. Now the second term is so small compared to the first that it can be neglected, when we have Ml/v_0, which when expressed in calories becomes Ml/v_0J.

It is this potential energy which constitutes the main part of the latent heat of vaporization; and it is this Ml/v_0J, which can be written $Ml\rho/J$; that I propose to use in place of the actual heat of vaporization at $15°$ C. The manner in which the latent heat is to be used in connexion with thermochemical data is as follows :—Suppose a solid element R to combine

with the solid element S to produce the solid compound RS
with evolution of heat q, then, to obtain the evolution of heat
when S as gas combines with R as gas to produce gaseous RS,
we must add the latent heat of vaporization of R and of S
and subtract that of RS: denoting these latent heats by L(R),
L(S), and L(RS), and the required heat of combination of
the gases by H(RS) we have

$$H(RS) = q - L(RS) + L(R) + L(S). \quad . \quad . \quad (15)$$

There remains now only to give tables of the experimental
data and the values of M^2l calculated from them by equations
(7), (11), and (13), and of $Ml\rho/J$ or L, the latent heat per
gramme-atom or gramme-molecule due to molecular force; L
is given in kilocalories. As the application of (11) to the
metals brings out some immediately interesting results, the
values for the metals will be taken first. In the metals the
ordinary atomic mass (weight) is taken for M.

TABLE I.

First family and Copper sub-family.

	Li.	Na.	K.	Rb.	Cs.	Cu.	Ag.	Au.
T	453	369	335	311	300	1330	1230	1310
M/ρ	11·9	23·7	45·4	56·1	70·6	7·2	10·2	10·2
M²l	4·1	8·6	16·2	21·2	27·6	11·1	15·9	18·7
L(kcal.)	8·3	8·6	8·5	9·0	9·3	36·6	37·0	43·5

Second family and Zinc sub-family.

	Be.	Mg.	Ca.	Sr.	Ba.	Zn.	Cd.	Hg.
T	1230	1023	900	800	748	690	590	234
M/ρ	5·6	13·8	25·4	34·9	36·5	9·1	12·9	14·7
M²l	5·8	13·9	24·5	34·0	35·9	7·3	9·7	4·8
L(kcal.)	24·5	23·9	23·0	23·2	23·4	19·1	17·9	7·8

Third family and Gallium sub-family.

	Al.			La.	Ga.	In.	Tl.
T	1123	......	......	710	303	449	563
M/ρ	10·6	......	......	22·3	11·7	15·3	18·1
M²l	11·9	......	......	23·5	4·1	8·8	14·3
L(kcal.)	26·8	......	......	25·2	8·4	13·6	18·8

Fourth family and Tin sub-family.

					Ce.		Sn.	Pb.
T	......	......	......	......	1000	......	503	599
M/ρ	......	......	......	......	21·0	......	16·1	18·1
M²l	......	......	......	......	27·9	......	10·9	15·3
L(kcal.)	......	......	......	......	31·6	......	16·1	20·1

Table I. (*continued*).

Fifth family and Arsenic sub-family.

	Di.	As.	Sb.	Bi.
T	1200	773	710	540
M/ρ	22·3	13·2	17·9	21·1
M²l	35·7	12·2	16·4	16·1
L(kcal.)	38·2	21·9	21·8	18·2

Eighth family—Iron, Palladium, and Platinum groups.

	Fe (Ni Co).	Pd (Ru Rh).	Pt (Os Ir).
T	2080	1775	2050
M/ρ	7·2	9·2	9·1
M²l	16·9	20·6	26·1
L(kcal.)	56·1	53·2	68·2

The first fact deserving attention in this table is that in each main family M$l\rho$/J or L, the latent heat of vaporization per gramme-atom due to molecular force, is constant. Thus, in the first family it is about 8·7, and in Cu and Ag about 37 or about four times the value in the main family ; in the second family the value is about 23·6, and for Zn and Cd about 18·5, which is much nearer to the value for the main family than was the case with Cu and Ag, a fact that is probably connected with the greater chemical similarity of Zn and Cd to the main family than is the case with Cu and Ag. The third main family is represented in the table by only two members, Al and La, which have practically the same value for L, the mean being 26·0, while in the related sub-family Ga has a value which is one third of this, just as that for Hg is one third of that in its main family ; In has a value which is nearly a half of that in the main family. At the fourth family we reach a point of transition, after which the sub-families have more the character of main families than the main families themselves. In the fourth main family we have but the one value, that for Ce, about 32, of which the value 16 for Sn in the sub-family is one half. In the fifth sub-family As, Sb, and Bi have nearly the same value, about 21, which is nearly one half of the 38 for Di in the main family. For Fe, Pd, and Pt the values are about 60. It is interesting to note how the latent heat per gramme-molecule due to molecular force increases with the valency or order of the main family. To bring this out more clearly the following little table is drawn up, containing in the first row the mean values of L, the latent heat per atom in each main family, and

in the second row the latent heat per equivalent, taking the family-number as the valency of the family.

TABLE I a.

Family number	1.	2.	3.	4.	5.	8.
Latent heat per gramme-atom	8·7	23·6	26·0	32·0	40	60
Latent heat per gramme-equivalent	8·7	11·8	8·7	8·0	8·0	7·5

These numbers in the second row show that the latent heat of vaporization per gramme-equivalent due to molecular force is nearly the same in all the main families, except the second, where it is half as large again as in the other main families ; as regards this relation the sub-family Zn and Cd would appear to take the place of the main family, for the value per equivalent is 9·2. As it has already been pointed out that the values per gramme-atom of most members of the sub-families are simple multiples or submultiples of those in the main family, the general principle can be enunciated for the metals :—The latent heat of vaporization per gramme-equivalent due to molecular force is approximately a constant or a simple multiple or submultiple of the constant.

The fact that we have been led to a general result such as this shows that the method of calculation has probably yielded correct relative values of the latent heat of vaporization due to molecular force ; it remains to see whether these are of about the right absolute magnitude. The only metal whose latent heat of vaporization we can determine independently by means of existing data is mercury; for all the terms in the thermodynamical relation $J\lambda = (v_3 - v_2)\theta \, dp/d\theta$ are known for mercury, $dp/d\theta$ being the rate of variation of the saturation pressure of the liquid with the temperature, v_2 and v_3 the volumes of a gramme of the substance as liquid and saturated vapour under the vapour-pressure at θ. With Regnault's data and the assumption that at the boiling-point of mercury a gramme-atom or 200 grammes of mercury would occupy the same volume as 2 grammes of hydrogen at the same temperature and pressure, Berthelot has calculated the atomic latent heat of mercury as 15·5 kilocalories. With the values of $dp/d\theta$ given by Ramsay and Young (Phil. Mag. 5th ser. vol. xxi.) I have calculated that 14 kilocalories would be the value, still on the above assumption as to the volume of saturated mercury vapour, but this volume is obviously too large ; and as it is a difficult enough matter to measure the true saturation volume of an ordinary vapour, it is evident that the experimental determinations hitherto made of the density of mercury vapour cannot be used in place of the

above assumption. From what is known of the saturation densities of ordinary vapours, it is likely that with the true volume of mercury vapour the value 14 for the latent heat would be reduced to at least 13, of which about one eleventh part is due to doing external work; so that the pure latent heat of liquid mercury is about 12 kilocalories for the gramme-atom. The latent heat of fusion of 200 grammes of solid Hg is ·6 kilocalories; so that the latent heat of vaporization of solid mercury is about 13 kilocalories per gramme-atom. The value calculated in Table I. for the latent heat due to molecular force is 7·8, and therefore the total latent heats would appear to be 1·6 times the tabulated values.

When the values of l are calculated for the metals by equation (7) with Quincke's values for the surface-tension, certain discrepancies with the values in Table I. appear, which were remarked on in "A Kinetic Theory of Solids" in an indirect manner. These discrepancies now appear to be due to varying molecular complexity in a few of the metals, and it would lead us too far to discuss them at present. In the case of compounds the two equations (7) and (13) give accordant results, to which we will proceed. We will first give a table for those binary compounds for which the data for both methods are available, so that the two sets of values for M^2l may be compared. In the following table the values of the surface-tension α_m are given in grammes weight per metre, and when taken from Quincke are denoted by Q and from Traube by T. The melting-points here and in the following table are taken chiefly from Carnelley (Journ. Chem. Soc. xxix., xxxiii., xxxv., and xxxvii.; Phil. Mag. 5th ser. vol. xviii.), and the densities from Clarke's 'Constants of Nature' and Landolt and Börnstein's *Tabellen*.

TABLE II.

	LiCl.	NaCl.	NaBr.	KF.	KCl.
α_m	12·1 Q.	11·6 T.	10·5 T.	14·2 T.	10·0 T.
ρ	2·00	2·15	3·00	2·45	1·98
M/ρ	21·2	27·2	34·4	23·7	37·6
T	870	1045	981	1060	1007
$M^2l(7)$	18·4	27·0	33·6	26·1	39·6
$M^2l(13)$	20·2	32·5	40·9	32·5	46·1

	KBr.	KI.	AgCl.	AgBr.	$CaCl_2$.
α_m	9·3 T.	8·5 T.	19·0 Q.	17·3 Q.	15·3 Q.
ρ	2·69	3·08	5·55	6·42	2·22
M/ρ	44·2	53·8	25·8	29·3	50·5
T	972	907	724	700	992
$M^2l(7)$	47·6	60·8	39·6	44·9	95·9
$M^2l(13)$	56·2	67·3	25·0	29·1	62·5

This table shows that for the first 7 compounds the values of M^2l by (13) are about 1·2 times those by (7), while for the last 3 they are only about ·6 times ; the values for the surface-tension of the last three are not so trustworthy as those of the first seven, in most of which Quincke's and Traube's values agree.   The above table could be extended by a number of data of Traube's relating to compounds of Na and K with compound acid radicals ; but the above table is representative, showing the average agreement of the two methods and the three worst cases of disagreement.   It is to be remembered that the experimental determination of α_m is difficult, and that the theories of the equations (7) and (13) are both only approximate ; and hence, all things considered, the above comparison ought to satisfy us that our equations can yield at least approximate relative values of M^2l for inorganic compounds.   In the next table are collected the data required in (13) for the haloid compounds of the metals and a few non-metals, along with the values of M^2l and of $Ml\rho/J$ or L, the latent heat of vaporization due to molecular force for a gramme-molecule.   Some of the data in Table II. are slightly different from the corresponding ones in Table III.

TABLE III.

	Li.				**Na.**			
	F.	Cl.	Br.	I.	F.	Cl.	Br.	I.
T	1070	870	820	719	1270	1045	981	901
M/ρ	11·3	21·3	28·0	38·4	16·4	27·3	33·4	43·5
M^2l	12·0	20·0	28·0	36·2	21·2	32·5	41·1	52·4
L(kcal.)	25·3	22·4	23·8	22·5	30·8	28·4	29·3	28·7

	K.				**Rb.**			
	F.	Cl.	Br.	l.		Cl.	Br.	I.
T	1060	1007	972	907	...	983	956	915
M/ρ	28·2	38·3	44·6	54·3	...	54·8	59·5	70·3
M^2l..............	32·7	46·0	55·7	66·7	...	69·2	76·9	90·8
L(kcal.)	27·6	28·6	29·8	29·2	...	30·1	30·8	30·8

	Cs.				**Be.**			
	Cl.	Br.	I.			Cl_2.	Br_2.	I_2.
T	...	904	879	869	...	870	870	770
M/ρ	...	76·2	80·9	91·7	...	39	51	66
M^2l	...	93·8	100·7	116·4	...	40·9	60·8	73·8
L(kcal.)	...	29·3	29·6	30 3	...	25·0	28·4	26·7

Mg.

	F$_2$.	Cl$_2$.	Br$_2$.	I$_2$.
T	1180	981	971	889
M/ρ	25·1	43·6	(56)	(71)
M^2l	33·6	53·2	73·8	94·2
L(kcal.)	31·8	29·1	31·4	31·6

Ca.

	F$_2$.	Cl$_2$.	Br$_2$.	I$_2$.
T	1170	992	949	904
M/ρ	24·8	50·0	60·3	(75)
M^2l	34·8	62·5	79·1	100·0
L(kcal.)	33·5	29·8	31·3	31·8

Sr.

	F$_2$	Cl$_2$.	Br$_2$.	I$_2$.
T	1170	1098	903	780
M/ρ	(31)	51·9	62·4	77·4
M^2l	47·6	75·5	80·9	92·0
L(kcal.)	36·6	34·7	30·9	28·3

Ba.

	F$_2$.	Cl$_2$.	Br$_2$.	I$_2$.
T	1180	1181	1085	929
M/ρ	36·2	54·1	70·3	(85)
M^2l	59·2	90·4	114·3	123·0
L(kcal.)	38·9	39·8	38·7	34·5

Zn. — Cd. — Hg.

	Cl$_2$.	Br$_2$.	I$_2$.	Cl$_2$.	Br$_2$.	I$_2$.	Cl$_2$.	Br$_2$.	I$_2$.
T	535	667	719	814	844	677	561	517	514
M/ρ	49·4	61·8	67·9	50·5	57·9	79·4	50·0	62·7	72·4
M^2l	34·8	59·2	73·8	56·2	72·1	82·8	40·9	50·3	59·2
L(kcal.)	16·8	22·8	25·9	26·5	29·6	24·8	19·5	19·1	19·4

Hg$_2$. — CuCl$_2$. — Cu$_2$.

	Br$_2$.	I$_2$.	CuCl$_2$.	Cl$_2$.	Br$_2$.	I$_2$.
T	678	562	773	707	780	874
M/ρ	76·6	85·1	44·0	55·7	60·5	86·3
M^2l	88·3	80·9	44·9	54·7	70·5	116·4
L(kcal.)	27·5	22·6	24·3	23·4	27·7	32·1

Ag. — Pb.

	Cl.	Br.	I.	Cl$_2$.	Br$_2$.	I$_2$.
T	724	700	800	769	769	653
M/ρ	25·8	29·7	41·8	47·8	55·2	75·5
M^2l	25·0	29·1	47·6	54·7	65·5	79·1
L(kcal.)	23·1	23·3	27·2	27·3	28·2	25·0

For the haloid compounds of the triad, tetrad, and pentad metals some data for the boiling-points T$_b$ are available, so that values of M^2l are calculable by equation (14), and accordingly in the next part of the table values of T$_b$ are given along with the values of M^2l calculated from them, the latter being denoted by M^2l (14). L is calculated from M^2l (13).

Table III. *(continued)*

	Al. Br_3	Al. I_3	C. Cl_4	C. Br_4	Si. Cl_4	Si. Br_4
T	363	398	—	364	—	260
T_b	533	623	351	462	331	426
M/ρ	105	155	94	98	112	124
$M^2l(13)$	56·2	98·2	(33·0)	54·7	(36·2)	49·0
$M^2l(14)$	65·5	114·3	39·6	53·2	43·4	62·5
L(kcal)	12·8	15·1	(8·4)	13·3	(7·7)	9·4

	Ti. Cl_4	Ti. Br_4	Sn. Cl_4	Sn. Br_4	Sn. I_4
T	...	312	260	303	419
T_b	408	503	388	474	568
M/ρ	108	142	118	132	133
$M^2l(13)$	(43·2)	68·9	44·9	64·0	94·2
$M^2l(14)$	51·8	84·7	54·7	73·8	90·4
L(kcal.)	(9·5)	11·6	9·1	11·5	16·9

	As. Cl_3	As. Br_3	As. I_3	Sb. Cl_3	Sb. Br_3	Sb. I_3	Bi. Cl_3	Bi. Br_3
T	250	295	419	345	363	438	503	480
T_b	405	493	677	496	549	693	703	749
M/ρ	82	85	104	74	88	103	69	80
$M^2l(13)$	28·0	38·4	70·5	36·0	49·0	73·8	51·8	60·8
$M^2l(14)$	39·6	50·3	82·8	43·4	57·8	84·7	57·8	70·5
L(kcal.)	8·1	10·8	16·1	11·6	13·3	17·1	17·9	18·1

In this part of the table it can be seen that the second values of M^2l are about 1·2 times the first, which is again confirmatory of the general fitness of our equations to give relative values of M^2l. There are a number of irregularities in the data of Table III., especially in connexion with the values of M/ρ for molecules containing more than two atoms of halogen : the differences in M/ρ for Br_3 and Cl_3, and for I_3 and Cl_3 are far from constant and far from three times the difference for Br and Cl, and I and Cl : a special study of the molecular domains of several of these compounds ought to be made. As to the laws reigning amongst the values of M^2l, they are specially discussed in a manuscript paper entitled " Further Studies on Molecular Force," which I hope will be published about the same time as this present paper : it is

shown there that if n is the valency of the metal R in a haloid compound RS_n, then $n^{\frac{1}{2}}(M^2l)^{\frac{1}{2}}$ is the sum of a constant for R and n times a constant for S. By determining mean values for these parts and then recalculating values of M^2l, it would be possible to smooth out some of the irregularities in the values of M^2l given in the table, but for the present I prefer to leave the values just as derived from the experimental data. Where a melting-point has been wanting in the last table, I have divided the value of M^2l derived from the boiling-point by $1\cdot2$ and enclosed it in brackets as a value derived from the melting-point, the value of $Ml\rho/J$ or L derived from this is also enclosed in brackets.

To determine how the values of the latent heat of vaporization per gramme-molecule due to molecular force stand in relation to experimental values of the total heat of vaporization, we have the following four values of molecular latent heats at boiling-point taken from Berthelot's *Mécanique Chimique*, namely, $7\cdot2$ for CCl_4, $6\cdot3$ for $SiCl_4$, $7\cdot6$ for $SnCl_4$, and $8\cdot4$ for $AsCl_3$; these should be diminished by about one eleventh of their value to remove the part due to external work, and then increased by the latent heat of fusion to give the molecular latent heat of vaporization of the solid without performance of external work. Let us suppose these two corrections to neutralize one another as latent heats of fusion are known to be small, then we have the comparison :—

...			CCl_4.	$SiCl_4$.	$SnCl_4$.	$AsCl_3$.
Experimental molecular latent heat	...		$7\cdot2$	$6\cdot3$	$7\cdot6$	$8\cdot4$
Calculated	,,	,, L. ...	$8\cdot4$	$7\cdot7$	$9\cdot1$	$8\cdot1$

This shows a fair general agreement between the two sets of values of L : in the first three cases the theoretical value is about $1\cdot2$ times the experimental ; while in the case of the one metal Hg, for which we could make the comparison, the experimental was found to be $1\cdot6$ times the theoretical. Accordingly it seems safest to multiply all our theoretical latent heats for the metals by $1\cdot6$, and divide the theoretical latent heats for compounds by $1\cdot2$, in order to be as little at variance as possible with the few direct measurements that are available. The next table contains the values of the latent heats per gramme-equivalent thus derived from those in Tables I. and III. by the factors $1\cdot6$ and $1/1\cdot2$:—

TABLE IV.

Values adopted in the rest of this Paper for the Heat of Vaporization in kilocalories of a gramme-equivalent.

Li, Na, K, Rb, and Cs, 13·9.   Cu and Ag, 59·2.

$\frac{1}{2}$Be, $\frac{1}{2}$Mg, $\frac{1}{2}$Ca, $\frac{1}{2}$Sr, and $\frac{1}{2}$Ba, 18·9. $\frac{1}{2}$Zn and $\frac{1}{2}$Cd, 14·8. $\frac{1}{2}$Hg, 6·2.

$\frac{1}{3}$Al, 14·4. $\frac{1}{2}$Pb, 16·1. $\frac{1}{3}$As, $\frac{1}{3}$Sb, and $\frac{1}{3}$Bi, 11·2.

Li.

Cl.	Br.	I.	Cl.	Br.	I.	Cl.	Br.	I.
18·7	19·8	18·7	23·7	24·4	23·9	23·9	24·9	24·3

(Na. and K. headings above last two groups)

Ag.   Cu(ous).

Cl.	Br.	I.	Cl.	Br.	I.
19·2	19·4	22·7	9·7	11·5	13·4

$\frac{1}{2}$Mg. $\frac{1}{2}$Ca. $\frac{1}{2}$Sr.

Cl.	Br.	I.	Cl.	Br.	I.	Cl.	Br.	I.
12·1	13·1	13·1	12·4	13·0	13·2	14·4	12·8	...

$\frac{1}{2}$Ba. $\frac{1}{2}$Zn. $\frac{1}{2}$Cd.

Cl.	Br.	I.	Cl.	Br.	I.	Cl.	Br.	I.
16·6	16·1	...	7·0	9·5	10·8	11·0	12·3	10·3

$\frac{1}{2}$Hg(ic). $\frac{1}{3}$Al. $\frac{1}{2}$Pb.

Cl.	Br.	I.	Cl.	Br.	I.	Cl.	Br.	I.
8·1	7·9	8·1	3·2	3·6	4·2	11·3	11·7	10·4

$\frac{1}{3}$As. $\frac{1}{3}$Sb. $\frac{1}{3}$Bi.

Cl.	Br.	I.	Cl.	Br.	I.	Cl.	Br.	I.
2·2	3·0	4·5	3·2	...	...	5·0	...	...

With these values and Thomsen's thermochemical data, we can now tabulate the heats of formation of the metallic haloid compounds when the reagents and products are both gaseous, for if q is the heat of formation of solid RS from solid metal R and solid halogen S, the latent heats of vaporization being L(RS), L(R), and L(S), then H(RS), the heat of formation of gaseous RS from gaseous R and gaseous S, is

$$H(RS) = q + L(R) + L(S) - L(RS).$$

Part I.

INORGANIC COMPOUNDS.

The haloid compounds of the metals have been chosen as a group in which thermochemical law might be expected to be most easily discernible. The following table of data for their heats of formation has been derived from Thomsen's data in the *Thermochemische Untersuchungen*, Band iii., where they

relate to a temperature of 18° C. and to the ordinary states
of all the substances at that temperature; that is to say, to the
gaseous state of Cl, the liquid of Br, and the solid of I, the
metals all being solid except Hg, and the compounds mostly
solid. To pass from Thomsen's data to those given in our
next table for heats of formation with reagents and products
all gaseous, it is necessary to subtract from his heat of forma-
tion of each equivalent of a compound the value given in
Table IV. for the latent heat of the equivalent, and then to
add the latent heat of an equivalent of the metal, and finally
to add the latent heat of vaporization of the halogen, which
for gaseous Cl is 0, for liquid Br is 3·6, and for solid I is 4·5.
In this way the following table has been prepared chiefly
from Thomsen's data, those for mercury being his later ones
(Abst. Journ. Chem. Soc. 1888); but the data for the bromide
and iodide of Li and Mg are due to Beketoff (Abst. Journ.
Chem. Soc. 1889, and Wied. *Ann., Beibl.* 16). The fourth
column of the table contains the differences of the heats of
formation of the chlorides and bromides, the fifth the differ-
ences for the chlorides and iodides, and the sixth the ratio
of the two sets of differences.

TABLE V.

Heat of Formation in kilocalories of gramme-equivalents of
the Haloid Compounds of the Metals, both reagents and
products being gaseous.

	Cl.	Br.	I.	Cl—Br.	Cl—I.	$\frac{(Cl-I)}{(Cl-Br)}$
Li............	89·0	77·7	60·9	11·3	28·1	2·5
Na	87·9	78·8	63·6	9·1	24·3	2·7
K............	95·6	87·9	74·2	7·7	21·4	2·8
Cu(ous) ...	82·3	76·3	66·5	6·0	15·8	2·6
Ag	69·4	66·1	54·8	3·3	14·6	4·4
$\frac{1}{2}$Mg.........	82·3	70·2	52·7	12·1	29·6	2·5
$\frac{1}{2}$Ca.........	91·1	79·9	63·8	11·2	27·3	2·4
$\frac{1}{2}$Sr	96·7	88·5	...	8·2	...	...
$\frac{1}{2}$Ba.........	99·6	91·4	...	8·2	...	...
$\frac{1}{2}$Zn.........	56·4	46·8	33·1	9·6	23·3	2·4
$\frac{1}{2}$Cd.........	50·4	43·7	33·4	6·7	17·0	2·5
$\frac{1}{2}$Hg(ic) ...	25·3	22·8	15·4	2·5	9·9	4·0
$\frac{1}{2}$Pb	46·2	40·2	30·1	6·0	16·1	2·7
$\frac{1}{3}$Al	61·6	54·3	38·2	7·3	23·4	3·2
$\frac{1}{3}$As	32·8	26·8	15·4	6·0	17·4	2·9
$\frac{1}{3}$Sb	38·5	...	...	...	...	...
$\frac{1}{3}$Bi	36·4	...	...	...	...	...

Additional data for H and for Ammonium Compounds, the
latter being formed from N and H and halogen all
gaseous :—

H	22·0	12·2	—·6	9·8	22·6	2·3
N,H$_4$	75·8	69·0	53·8	6·8	22·0	3·3

The first conclusion to be drawn from inspecting this table is one unfavourable to the view of those who hold that each atom in passing from the elementary to the combined state evolves a fixed amount of heat irrespective of the atoms with which it combines ; or, in other words, that the heats of combination can be separated into thermochemical moduluses or parameters characteristic of each element : for if this were so, then the columns headed $Br-Cl$ and $I-Cl$ in this table ought to be constant, whereas the large variations in these columns establish the fundamental principle that the amount of heat evolved on the combination of two atoms depends on certain mutual relations of the atoms, a point that Beketoff appears to have been most strenuous in insisting on, and also Berthelot. Now in the case of compounds formed in dilute solution, it has been proved that in a large number of cases the heat of formation is independent of mutual relations between the reacting atoms, and may be expressed as the sum of moduluses characteristic of each; and thus it will be seen that our first result is calculated to throw new light on the nature of solution, for it shows that in the process of solution certain mutual relations of the atoms of the dissolved molecule cease to be operative.

The second conclusion which can be drawn from this table is that the ratio of $Cl-I$ to $Cl-Br$ is nearly constant, because the large departures in the case of Ag and Hg do not count for anything, seeing that with them $Cl-Br$ is so small that its value is relatively greatly altered by relatively small unavoidable errors in the values for Cl and Br respectively. Indeed with the existing uncertainties in our calculations of the latent heats of vaporization of solids, it is obvious that we can hardly ascertain whether the departures of the ratio from constancy are real or due to errors, but under the circumstances the approximation to constancy is close enough to warrant our assuming it to be probably a law of nature. This, then, we take to be our second result, that such ratios as those tabulated under the heading $(Cl-I)/(Cl-Br)$ are constant, and it must be our first business to inquire what may be the meaning of such a result. The simplest way of expressing a dependence of the heat of combination on mutual relations of the reacting atoms is to suppose that $H(RS)$ is of the form $(R)+f(RS)+(S)$ where (R) depends on R alone, (S) on S alone, and $f(RS)$ on both R and S. Suppose S_1 to stand for Cl, S_2 for Br, and S_3 for I, then

$$\frac{H(RS_1)-H(RS_3)}{H(RS_1)-H(RS_2)} = \frac{(S_1)-(S_3)+f(RS_1)-f(RS_3)}{(S_1)-(S_2)+f(RS_1)-f(RS_2)};$$

but this ratio has just been proved to be probably constant, that is independent of R : which implies that

$$(S_1) - (S_3) = 0 = (S_1) - (S_2),$$

and that $f(RS)$ can be resolved into two factors, one depending on R only, and the other on S only. Let

$$f(RS) = \psi(R)\psi(S),$$

then the last equation becomes

$$\frac{H(RS_1) - H(RS_3)}{H(RS_1) - H(RS_2)} = \frac{\psi(S_1) - \psi(S_3)}{\psi(S_1) - \psi(S_2)},$$

which is of course independent of R.

Thus for the halogens, as the mean value for the ratio in the last table (excluding Ag and Hg) is 2·6, we have the following fundamental equations :—

$$(Cl) = (Br) = (I) \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$\psi(Cl) - \psi(I) = 2\cdot6\{\psi(Cl) - \psi(Br)\}. \quad . \quad . \quad . \quad (2)$$

The third result obtained from Table V. is that the columns headed Cl−Br and Cl−I, being the values of

$$\psi(R)\{\psi(Cl) - \psi(Br)\} \text{ and } \psi(R)\{\psi(Cl) - \psi(I)\},$$

afford a clue to the law of $\psi(R)$. In order to deal with as large numbers as possible, and so reduce the relative importance of errors in the data, we will add the two columns of differences; and since the numbers in the Cl−I column are on the average 2·6 times those in the Cl−Br column, the result of adding is to get $3\cdot6\psi(R)\{\psi(Cl) - \psi(Br)\}$, the values of which are given in the following table, arranged in order of magnitude :—

TABLE VI.

	$\frac{1}{2}$Mg.	$\frac{1}{2}$Ca.	Li.	Na.	$\frac{1}{2}$Zn.	$\frac{1}{3}$Al.	K.
	41·7	38·5	34·4	33·4	32·9	30·7	29·1
Multiples	41·8	38·0	34·2	34·2	34·2	30·4	30·4
of 3·8	11	10	9	9	9	8	8

	$\frac{1}{2}$Cd.	$\frac{1}{3}$As.	$\frac{1}{2}$Pb.	Cu.	Ag.	$\frac{1}{2}$Hg.
	23·7	23·4	22·1	21·8	17·9	12·4
Multiples	22·8	22·8	22·8	22·8	19·0	11·4
of 3·8	6	6	6	6	5	3

The second row of numbers is a series of multiples of 3·8, and a comparison of the two rows shows that the values of $3\cdot6\psi(R)\{\psi(Cl) - \psi(Br)\}$ approximately form a series of

multiples of 3·8; so that the values of $\psi(R)\{\psi(Cl) - \psi(Br)\}$ are represented by the form $N \times 1·06$, in which N is an integral number characteristic of each metal: as $\psi(Cl) - \psi(Br)$ remains constant, the values of $\psi(R)$ for the metals are proportional to a series of integral numbers.

It will be well to arrange these integral numbers according to the natural classification of the elements; the values for $\frac{1}{2}Sr$ and $\frac{1}{2}Ba$ can be derived from the values for $Cl - Br$ in Table V., they are 8 and 8.

Table VII. —

Integers proportional to $\psi(R)$ for the Metals.

Li.	Na.	K.	Cu.	Ag.	$\frac{1}{2}Mg.$	$\frac{1}{2}Ca.$	$\frac{1}{2}Sr.$
9	9	8	6	5	11	10	8

$\frac{1}{2}Ba.$	$\frac{1}{2}Zn.$	$\frac{1}{2}Cd.$	$\frac{1}{2}Hg.$	$\frac{1}{2}Pb.$	$\frac{1}{3}Al.$	$\frac{1}{3}As.$
8	9	6	3	6	8	6

This table shows that in each main family the integer decreases with increasing atomic mass : if the value for $\frac{1}{2}Sr$ were 9 the series of values in the Mg family would run 11, 10, 9, 8 ; in the zinc family the series is regular, namely, 9, 6, and 3 ; but the data are not extensive enough or accurate enough to make sure whether in each natural family the integers form an arithmetical progression ; however, the data of the last table are very suggestive of the probable truth of the following addition to our third result, namely, that the values of $\psi(R)$ in each family form an arithmetical progression.

An inspection of the heats of formation of the iodides in Table V. leads to our fourth conlusion, for it is noticeable that there is a large range in the values from 74·2 for KI to $-·6$, or say 0 for HI. This makes it probable that in $(R) + f(RI) + (I)$ the value of the constant part (I) is small compared to the variable part $(R) + f(RI)$: we are therefore encouraged to assume $(I) = 0$. It must be remembered that (I) denotes that part of the heat of combination of a gramme-atom of iodine which is independent of the nature of the atoms with which it is uniting, the iodine being supposed gaseous at 18° C., and therefore having a diatomic molecule : thus (I) has nothing to do with the heat of dissociating the iodine molecule into atoms, which on thermodynamical grounds Boltzmann has calculated as 14·2 kcal. per gramme-atom (Wied. *Ann.* xxii.). It appears, then, that we cannot be far wrong in putting $(I) = 0$, and then from the equation (1) above we must put $(Cl) = 0$ and $(Br) = 0$. In explanation of this result to which our assumption has led, it may be urged

that in the halogens as elements, atom is combined with atom to form the diatomic molecule, in contrast to the state of affairs known for at least the five monatomic metals Na, K, Zn, Cd, and Hg. This difference between the atoms of halogen and of metals suggests that the relation

$$(I) = (Br) = (Cl) = 0$$

does not by symmetry necessitate that for the metals $(R) = 0$. But for hydrogen, in which the molecule is diatomic, we ought by symmetry to expect $(H) = 0$: hence, as $H(HI)$ is small, say zero, we must have either $\psi(I) = 0$ or $\psi(H) = 0$, or both are zero. Of these alternatives the preferable one is that which makes $\psi(I) = 0$, because of the comparative chemical inertness of iodine; and, accordingly, the heats of formation of the iodides given in Table V. may be taken as approximate values of (R). For $\frac{1}{2}SrI_2$ and $\frac{1}{2}BaI_2$ the data are lacking, but may be approximately derived from those for the chlorides by subtracting $2\cdot6 \times 9 \times 1\cdot06$ and $2\cdot6 \times 8 \times 1\cdot06$, when we get $71\cdot9$ and $77\cdot5$; but it should be noted that Thomsen states that the absolute values for the heats of formation of all the Ba compounds are uncertain, because he was unable to get pure enough barium to give a reliable initial datum, and preferred to assign a value for the formation of the hydrate by analogy with the data for Mg, Ca, and Sr : on this account the value for $\frac{1}{2}BaI_2$ is uncertain and will be marked with a ?. The next table contains the values of the heats of formation of the iodides arranged in order of magnitude, and in the second row these have been divided by $3\cdot8$.

TABLE VIII.

Approximate Values of (R) for the Metals.

	$\frac{1}{2}Ba.$	K.	$\frac{1}{2}Sr.$	Cu.	$\frac{1}{2}Ca.$	Na.	Li.
(R)	77·5 ?	74·2	71·9	66·5	63·8	63·6	60·9
(R)/3·8 ...	20·4 ?	19·4	18·9	17·4	16·8	16·7	16·0

	Ag.	$\frac{1}{2}Mg.$	$\frac{1}{3}Al.$	$\frac{1}{2}Cd.$	$\frac{1}{2}Zn.$	$\frac{1}{2}Pb.$	$\frac{1}{2}Hg.$	$\frac{1}{3}As.$
(R)	54·8	52·7	38·2	33·4	33·1	26·7	15·4	15·4
(R)/3·8 ...	14·4	13·9	10·0	8·8	8·7	7·0	4·0	4·0

Several of the numbers in the second row will be seen to be close to the values 4, 9, and 16, that is 2^2, 3^2, and 4^2, a fact which suggests that for the metals (R) is a quadratic function of the numbers 1, 2, 3, 4, and so on. In the magnesium family we find on passing from $\frac{1}{2}Mg$ to $\frac{1}{2}Ca$ an increase of $2\cdot9$, and from $\frac{1}{2}Ca$ to $\frac{1}{2}Sr$ $2\cdot6$, which is nearly the same ; on

passing from the value for $\frac{1}{2}$Sr to that for $\frac{1}{2}$Ba the increase is
only 1·0, but the value for $\frac{1}{2}$Ba is quite uncertain. The
differences for the three members of the Li family are not
regular, being ·7 from Li to Na, and 2·7 from Na to K, the
latter being close to the values 2·9 and 2·6 in the Mg family.
Both in the Li and the Mg families (R) increases with
increasing atomic mass ; but in the Cu and Ag family we find
a diminution of (R) in passing from Cu to Ag, the decrease
in (R)/3·8 being 3·0, which is close to the 2·9, 2·6, and 2·7
already found in the other families. It is interesting to find
on passing from Zn to Cd that the value of (R) is stationary,
for like Cu and Ag these two metals form a subfamily, and
might be expected like them to have (R) diminishing with
increasing atomic mass, but they are much more closely
related to their main Mg family, which might be expected to
give increasing (R) with increasing atomic mass ; the two
tendencies appear to neutralize one another and leave (R)
stationary. More data are required before the law regulating
(R) can become clear, and these are specially desirable for
the compounds of the rarer metals of the Li and Be families,
that is for the haloid compounds of Rb and Cs, and of Be and
Ba. Beketoff has made determinations for the compounds of
Rb in solution, but I have not seen any determinations of the
heat of solution of RbCl, RbBr, and RbI ; Petersen has also
made some determinations for Be, but not complete. It can
be seen that the most important thermochemical experimental
work for immediate requirements is the determination of
such hitherto undetermined data as will enable a table to be
drawn up showing the heats of formation of the haloid com-
pounds of all the metals, reagents and products being in the
gaseous state.

I have not discussed the available data for the heat of for-
mation of the nitrates, sulphates, and carbonates of the metals,
because it seems desirable that the simpler problem of binary
compounds should be carried further towards solution before
the more complex one is handled. A few data for the fluorides
are available for discussion, for Guntz (*Compt. Rend.* xcvii.)
has given values for the heat evolved when gaseous HF acts
upon the solid hydrates to produce solid fluorides and solid
H_2O. Let R be an equivalent of any metal, and A the
quantity of heat found by Guntz, then we have the thermo-
chemical equation

$$\text{ROH solid} + \text{HF gas} = \text{RF solid} + H_2O \text{ solid} + A.$$

From Thomsen's data we can get the values of B in the
equation

$$\text{R solid} + O + H = \text{ROH solid} + B,$$
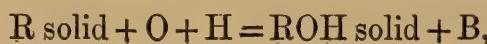
and Berthelot and Moissan (*Compt. Rend.* cix.) have given C in

then
$$H + F \text{ gas} = HF \text{ gas} + C ;$$

$$R \text{ solid} + O + 2H + F \text{ gas} = ROH \text{ solid} + HF \text{ gas} + B + C,$$

and therefore
$$= RF \text{ solid} + A + B + C + H_2O \text{ solid} ;$$

but
$$O + 2H = H_2O \text{ solid} + D,$$
therefore
$$R \text{ solid} + F \text{ gas} = RF \text{ solid} + A + B + C - D.$$

The value of D is $68\cdot4 + 1\cdot4$ or $69\cdot8$, that of C is $37\cdot6$, and the following are the values of A and B :—

	Na.	K.	½Mg.	½Ca.	½Sr.	½Ba.
A	39·9	38·2	28·4	33·3	35·9	35·7
B	101·9	103·2	108·6	107·4	107·2	107·4

The latent heats of vaporization of the gramme-molecule of the fluorides are :—

Na.	K.	½Mg.	½Ca.	½Sr.	½Ba.
25·7	23·0	13·2	14·0	15·2	16·2

With these numbers the following heats of formation of the fluorides (reagents and products gaseous) have been obtained, and along with them are given their differences from the heats of formation of the chlorides, and the same differences for the chlorides and bromides :—

TABLE IX.

Heat of Formation of Fluorides, reagents and products gaseous.

	F.	F−Cl.	Cl−Br.
Na	97·8	9·9	9·1
K	100·1	4·5	7·7
½Mg	110·5	28·2	12·1
½Ca	113·5	22·4	11·2
⅓Sr	114·6	17·9	8·2
½Ba	113·6	14·0	8·2

According to our previous experiences we should expect the ratios of the differences F−Cl and Cl−Br to be constant, but they are far from being so; perhaps the irregularities are due to polymerization not taken into account in our calculations, because the strong combination between KF and HF to form KHF_2 is suggestive of a molecular formula K_2F_2 in place of KF. All that can be said of the two columns of differences

is that they vary in the same direction, that is to say, when Cl — Br diminishes F — Cl also diminishes. The fluorides do not give us any light at present, but it is evident that they form a very interesting group for thermochemical study. The oxides, sulphides, and selenides have not been considered in this paper, because their melting-points being unknown it is not possible to calculate their latent heats.

In the next part of this paper it will be shown how the principles ruling amongst inorganic compounds apply to the organic.

PART II.

ORGANIC COMPOUNDS.

The method which it is proposed to pursue in this part is simply to follow Thomsen in the successive steps of his generalizations in the fourth volume of his *Thermochemische Untersuchungen*, and to retain the greater part of his conclusions which are valid, while rejecting a few that are invalid, or putting a more valid interpretation upon them than was given to them by their discoverer. I have gathered from abstracts of papers published by Thomsen since the fourth volume of his great work, that he has himself abandoned some of the unsound conclusions. Armstrong has supplied English chemists with a sketch of Thomsen's theory of the thermochemistry of organic compounds in the Philosophical Magazine (5th series, vol. xxiii.), along with some criticism of some of the more extremely heterodox opinions on chemical constitution advanced by Thomsen. This second part of the present paper will form another similar sketch, the repetition being unavoidable in the interests of clearness and the new point of view.

Thomsen confined his attention to the data determined by himself for about 120 compounds, apparently because he had taken some trouble to devise a method of determining the heat of combustion of all substances as vapours, and wished to avoid making uncertain corrections for latent heat in the determinations of others who experimented on liquids and solids. From the heat of combustion as vapour at the boiling-point he is able, by approximate values of specific heats, to make the small correction necessary for the heat of combustion of the substance as vapour (gas) at 18° C. at the constant pressure of one atmo. These results he gives to the nearest ten calories; that is, to the nearest hundredth of a kilo-calorie in the heat of combustion of a gramme-molecule. But as different experimenters often differ by some kilo-

calories in the values which they obtain for the heat of combustion of a gramme-molecule of the same substance, it cannot be conceded that Thomsen's values attain an accuracy warranting the retention of his figures for hundredths of kilocalories, especially as his desire to obtain heats of combustion for substances only in the form of vapours constrained him to use experimental methods liable to greater experimental error than belongs to other methods. Accordingly Thomsen's numbers will be reproduced here only to the nearest tenth of a kilocalorie for the gramme molecule. But it must be remembered that even this degree of refinement is only retained because, the experiments being all carried out by the one experimenter, there is a chance that even if absolute values are not correct to this degree the differences for related bodies may often be correct to the nearest tenth of a kilocalorie per gramme-molecule. In calculating heats of formation from amorphous carbon and the other elements as gases at 18° C. and a pressure of one atmo from the heats of combustion, Thomsen uses for the heat of formation of CO_2 the value 96·96 kcal., and for the formation of liquid H_2O from its elements 68·36. To obtain the heat of formation of the gramme-molecule at constant volume, it is necessary to subtract $·29(n-2)$ kcal., where n is the number of atoms other than C in the molecule. It must be remembered that the heat of formation of the molecule of an organic compound is, as a rule, only a fraction of its heat of combustion : for instance, the heat of combustion of C_6H_{14} is about 1000, while the heat of formation is about 60 ; and this fact is the main cause of the difficulty in the advance of organic thermochemistry, for a relatively small error in a heat of combustion becomes relatively large in a heat of formation. We shall have occasion to illustrate this difficulty in the sequel by examples of the conflict of experimental authority in values of heats of formation.

In discussing Thomsen's results we will use the same notation as in Part I. to express the same ideas, namely, that the heat evolved on the combination of two atoms R and S can be analysed into three parts : one (R) depending on R only, another (S) depending on S only, and the third $f(RS)$ depending on both. At the very outset of organic thermochemistry a most interesting question arises as to this mutual action of atoms, for when three atoms R, S, and T react we might expect to have the equation

$$H(RST) = (R) + (S) + (T) + f(RS) + f(RT) + f(ST) ;$$

but if, according to the theory of radicals, ST forms a radical

such as OH in KOH, then K is not supposed to be in the same intimate relations with H as it is with O, so that in the last equation $f(\text{RT})$ would not be expected to be comparable to $f(\text{RS})$ or $f(\text{ST})$; and it may be stated that the most important and broadest generalization underlying Thomsen's results is, that the mutual effect of atoms which are not directly united with one another according to the ordinary scheme of formulæ, may be neglected with at least a close first approximation to the truth.   The mutual effect of un-connected atoms in the organic molecule must therefore in most cases belong to the region of second approximations. and though of the highest interest need hardly be looked for systematically until the accuracy of experimenting is carried still higher ; but a few striking cases will force themselves on our notice even in the present inquiry.   There is no occasion to prove by illustrative examples the approximate thermochemical independence of unconnected atoms in the molecule, because, as Thomsen's whole system depends on it, the whole of the rest of this paper will be illustrative of it. Thomsen's method of expressing his results involve the prin-ciple, for he assigns a thermal value to each bond in the graphical formula of a molecule and determines it for several. Thus, for instance, the heat of formation of C_2H_5OH from atoms of C, O, and H is regarded as the sum of a thermal value for the bond joining the two C atoms to one another, for the five bonds joining H to C, for the one joining O to C, and for one joining O to H ; and there is assumed to be no thermal contribution due to any relations of the O atom to the five atoms of alkyl hydrogen or of the hydroxyl hydrogen to the carbon : that is to say, it is assumed that all mutual influences except those due to direct connexion can be neglected.

There are some instances, as in the ammonium compounds, where the mutual influences of unconnected atoms are of the highest importance ; for the four atoms of H in NH_4Cl seem to affect profoundly the relation of the N atom to the Cl, so that it is quite different from the relation in NCl_3.   But these exceptional cases will not be studied in the present paper, unless when unavoidable.

We can now proceed to take the subject matter of Thomsen's conclusions section by section.

1. *The effect of* CH_2 *in the Heat of Combustion of Homo-logous Series.*—Each addition of CH_2 in a series increases the heat of combustion by an average amount of 157·9 kcal.; only 5 out of 44 values are more than 1 per cent. different from this average.   Accordingly, as a first approximation it

may be taken that the heat of combustion of CH_2 is constant, and therefore the heat of formation and attachment of CH_2 to a nucleus is to be taken as constant. Let CH_2 be attached to any nucleus X, then the heat of formation of XCH_2 is

$$H(X, C, H_2) = (X) + (C) + 2(H) + f(XC) + 2f(CH),$$

where (X) is the heat of formation of X, so that for the heat of formation and attachment of CH_2 to X we have

$$(C) + 2(H) + f(XC) + 2f(CH),$$

which we have just seen is independent of X; so that $f(XC)$ is independent of X—that is, it is constant; and as the CH_2 in homologous series is always attached to a C atom in the nucleus X in such a way as to increase the total number of single bindings between carbon atoms by one, we can write the constant $f(XC)$ as $f(C \cdot C)$, the dot denoting a single binding. The heat of combustion of CH_2 in a compound is therefore

$$3(O) + f(CO_2) + f(H_2O - f(C \cdot C) - 2f(CH) ;$$

and taking the mean value 157·9, we have

$$3(O) + f(CO_2) + f(H_2O) - f(C \cdot C) - 2f(CH) = 157 \cdot 9. \quad (1)$$

2. *Equality of the four Affinities of Carbon.*—The four bonds of carbon are proved to have the same thermal value by the fact that the successive replacement of the four H atoms of CH_4 to produce CH_3CH_3, $CH_2(CH_3)_2$, $CH(CH_3)_3$, and $C(CH_3)_4$ causes a constant increase in the heat of combustion at each replacement.

3. *The Heat of Combustion of Carbon in its Compounds.*— By comparing the heats of combustion of such saturated and unsaturated molecules as CH_4 and C_2H_4, or C_2H_5OH and C_3H_5OH, namely 211·9 for CH_4 and 333·3 for C_2H_4, it is shown that the heat of combustion of the surplus carbon atom is on the average 121·1, while the heat of combustion of a gramme-atom of solid amorphous carbon is 96·96. The difference between the two cases is that in the first the carbon atom, according to Thomsen's mode of expression, must be separated from a gaseous molecule by breaking a double binding and then combined with oxygen; while in the second case the atom has first to get its share of latent heat for the vaporization of the molecule and then the heat necessary to break it away from the molecule, after which it is combined with oxygen with the evolution of heat, the algebraic sum of all the thermal effects being 96·96 in this case and 121·1 in the former. Thomsen denotes the heat of combustion of the supposed isolated carbon atom by the symbol

$f \cdot c$, and the heat representing the work to be done in break-ing the single, double, and treble bindings of two carbon atoms by v_1, v_2, and v_3. The result just given is expressed by the equation

$$f \cdot c = 121 \cdot 1 + v_2,$$

which in our notation is

$$2(O) + f(CO_2) - f(C:C) = 121 \cdot 1. \qquad . \qquad . \quad (2)$$

From the heats of combustion of allylene, $CHCCH_3$, and ethylene, CH_2CH_2, namely $467 \cdot 5$ and $333 \cdot 3$, Thomsen gets the relation

$$f \cdot c = 134 \cdot 2 - v_1 - v_3 + v_2,$$

which in our notation is

$$2(O) + f(CO_2) - f(C \cdot C) - f(C:C) + f(C:C) = 134 \cdot 2. \quad (3)$$

4. *The Influence of Hydrogen.*—Compounds such as C_2H_4 and C_2H_6, or C_2H_3Cl and C_2H_5Cl, in which the addition of 2H to the unsaturated one produces the saturated, show a difference in their heat of combustion amounting to $37 \cdot 3$, or in symbols,

$$(O) + f(OH_2) - f(C \cdot C) - 2f(CH) + f(C:C) = 37 \cdot 3. \quad . \quad (4)$$

But where the added hydrogen takes up a different function, as in the passage from an aldehyde to an alcohol, the increase in the heat of combustion is $57 \cdot 8$, whence the equation

$$(O) + f(OH_2) + f(C:O) - f(CH) - f(C \cdot O) - f(OH) = 57 \cdot 8. \quad (5)$$

Going back to the case of hydrogen of constant function, Thomsen remarks that the sum of $121 \cdot 1$ for C and $37 \cdot 3$ for H gives $158 \cdot 4$, which is the heat of combustion of CH_2 ; that is, if we add our equations (2) and (4) we get

$$3(O) + f(CO_2) + f(OH_2) - f(C \cdot C) - 2f(CH) = 158 \cdot 4,$$

which is practically identical with (1), as it ought to be.

5. *Heat of Combustion of the isolated Carbon Atom.*—This is the particular section whose invalidity has seemed to detract from the value of Thomsen's discoveries, because so much of the rest of his work depends on it. Fortunately it so happens that though the reasoning of the section is unsound, its conclusion when properly interpreted is probably correct. Thomsen supposes an atom of C to be introduced into CO_2 in such a way as to produce the compound $OC = CO$; and this compound by reason of its double binding would, accord-ing to section 3, have a heat of combustion greater than that

of CO_2 by 121·1 ; but the heat of combustion of CO_2 is nothing, therefore the heat of combustion of $OC=CO$ would be 121·1. Now this compound may be supposed to be burnt by being first split into two molecules of CO, which will double the gaseous volume, and then being burnt as $2CO$, which is known to give out 135·9 kcal. Accordingly 135·9 minus ·58 for the doubling of the volume minus v_2 for breaking the double binding must be equal to 121·1, or, in symbols $121·1 = 135·3 - v_2$, that is, $121·1 + v_2 = 135·3$. But by section 3, $121·1 + v_2$ is $f.c$, the heat of combustion of an isolated carbon atom. Thus we have the two results,

$$v_2 = 14·2,$$

$$f\ c = 135·3.$$

This curious piece of reasoning appears to have furnished the values of two fundamental thermochemical constants by the artifice of imagining an unknown compound $OC=CO$ and asserting that the heat of combustion of CO_2 is nothing. These processes involve assumptions which may or may not be legitimate or necessary ; but it is certainly necessary that we should know what they are, and realize what we are committing ourselves to. We can do so by stating in our symbols the steps of the reasoning. The combustion of $2CO$ to produce $2CO_2$ at constant volume is expressed by

$$2(O) + 2f(CO_2) - 2f(CO) = 135·3 ; \quad . \quad . \quad . \quad (6)$$

and from equation (2),

$$2(O) + f(CO_2) - f(C:C) = 121·1 ;$$

hence

$$f(CO_2) - 2f(CO) + f(C:C) = 14·2. \quad . \quad . \quad . \quad (7)$$
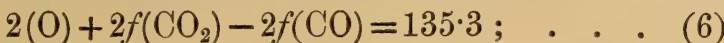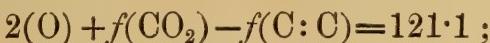
This corresponds to Thomsen's assertion $v_2 = 14·2$; and as his v_2 is identical with $f(C:C)$, we see that his equation $v_2 = 14·2$ is true only on condition that $f(CO_2) = 2f(CO)$. This is a legitimate assumption to make, if it is carefully tested by its consequences. If it is true, then $f(C:C) = 14·2$, and equation (6) reduces to the form $2(O) + f(CO_2) = 135·3$, which Thomsen calls the heat of combustion of the supposed isolated carbon atom. But it is not so : it is only a portion of that heat the whole of which in our notation is $(C) + 2(O) + f(CO_2)$. In Part I. we saw that $(Cl) = (Br) = (I) = 0$, and supposed this to be due to the fact that in the molecule of Cl two atoms are combined. If this is the true reason (O) is also zero, and then

$$(fCO_2) = 135·3 = 2f(CO). \quad . \quad . \quad . \quad . \quad (7a)$$

6. *Heat of Formation of the Carbon Molecule from its Atoms.*—If 135·34 is taken to be the heat of combustion of an isolated carbon atom, and 96·96 that of an atom as it exists in solid amorphous carbon, then 38·4 is the heat required to vaporize a gramme-atom of solid amorphous carbon and resolve it into atoms; so that if there are n atoms of carbon to the molecule, the heat required to vaporize and dissociate a gramme-molecule of solid amorphous carbon is $n \times 38\cdot4$.   According to our mode of expression this reasoning becomes

$$2(O) + 2f(CO_2) - 2f(CO) = 135\cdot34, \quad . \quad . \quad . \quad (8)$$

$$2(O) + 2f(CO_2) + (C \text{ solid}) = 96\cdot96;$$

therefore

$$f(CO_2) - 2f(CO) - (C \text{ solid}) = 38\cdot38. \quad . \quad . \quad (9)$$

The symbol (C solid) stands for that part of the change of energy of a gramme-atom passing from the amorphous solid state into a gaseous compound which is independent of the nature of the elements to which the C atom is united.   If $f(CO_2) = 2f(CO)$, then $-(C \text{ solid}) = 38\cdot4$; so that on this assumption the number 38·4 has a different signification from that assigned to it by Thomsen.

7. *Heat of Combination of Carbon with Hydrogen.*—The principle on which Thomsen proceeds in the rest of his investigations in vol. iv. of the *Thermochemische Untersuchungen* is always to add to the heat of formation of a compound from solid amorphous carbon 38·4 for each atom of carbon, so as to get what he calls the heat of formation from isolated carbon atoms.   But it appears from his later writings that he considers it not to be possible from existing data to obtain the heat required to vaporize and dissociate the gramme-molecule of solid amorphous carbon, so that he would appear to allow now that the addition of 38·4 for each carbon atom serves no good end.   But we have seen that, with the not unnatural assumption that $f(CO_2) = 2f(CO)$, the number 38·4 has the important signification $-(C \text{ solid})$, and therefore its addition for each atom of solid carbon taking part in the formation of a compound molecule serves the important purpose of eliminating the function $-(C \text{ solid})$ from the expression for the heat of formation : we shall see this purpose illustrated by following Thomsen in this seventh section.   The heat of formation of CH_4 from solid carbon and gaseous hydrogen is 21·2 ; adding 38·4 we get 59·6, which was formerly regarded by Thomsen as the heat of formation of CH_4 from isolated carbon atoms and hydrogen

molecules ; in our notation we have

$$4(H) + 4f(CH) + (C \text{ solid}) = 21 \cdot 2,$$

$$- (C \text{ solid}) = 38 \cdot 4 ;$$

$$\therefore \ 4(H) + 4f(CH) = 59 \cdot 6. \quad . \quad . \quad . \quad (10)$$

Or, strictly,

$$4(H) + 4f(CH) + f(CO_2) - 2f(CO) = 59 \cdot 6.$$

As H_2 is a diatomic molecule it may be that $(H) = 0$ similarly to the cases of Cl, Br, and I, and then equation (10) becomes

$$4f(CH) = 59 \cdot 6. \quad . \quad . \quad . \quad . \quad (11)$$

The case of C_2H_4 ought to work out to practically the same result as that of CH_4 ; following Thomsen we will take it as another example :—

$$2(C \text{ solid}) + 4(H) + f(C:C) + 4f(CH) = -3 \cdot 3, \ . \ (12)$$

$$-2(C \text{ solid}) + f(CO_2) - 2f(CO) \qquad = 76 \cdot 8,$$

and by (7)

$$f(C:C) + f(CO_2) - 2f(CO) \qquad = 14 \cdot 2.$$

Therefore adding the first two equations and subtracting the third,

$$4(H) + 4f(CH) = 59 \cdot 3.$$

8. *Fundamental Thermochemical Constants.*—From all his data for the hydrocarbons Thomsen determines average values of his constants v_1, v_2, and v_3, the thermal values of single, double, and treble bindings of carbon atoms, and for r the heat developed when an atom of hydrogen is forced out of a molecule of hydrogen and united to an isolated atom of carbon ; he gets a series of equations, such as

for CH_4 $\qquad\qquad 59 \cdot 6 = 4r,$

for C_2H_6 $\qquad\qquad 104 \cdot 2 = 6r + v_1,$

for C_3H_8 $\qquad\qquad 148 \cdot 5 = 8r + 2v_1,$

and so on, for 6 paraffins in all. Applying the method of least squares to the six equations for two unknowns he finds $2r = 30 \cdot 1$ and $v_1 = 14 \cdot 0$, which is nearly the same as the value already found for v_2, namely $14 \cdot 2$.

To find v_3 he uses the data for acetylene C_2H_2, allylene C_3H_4, and dipropargyl C_6H_6, which give the equations :—

$$29 \cdot 0 = 2r + v_3,$$
$$74 \cdot 6 = 4r + v_3 + v_1,$$
$$133 \cdot 1 = 6r + 2v_3 + 3v_1,$$

which, with the above values of r and v_1, give for v_3 the values $-1 \cdot 1$, $\cdot 4$, and $\cdot 2$, which are small, and the average of which may be taken as 0.

The values which in our notation correspond to these may be got as follows :—first, on looking at the strict form of equation (10) we see that

$$4(H) + 4f(CH) + f(CO_2) - 2f(CO) = 59 \cdot 6 = 4r ; \quad . \quad (13)$$

again, for C_2H_6 we have

$$2(C \text{ solid}) + 6(H) + f(C \cdot C) + 6f(CH) = 27 \cdot 4, \quad . \quad (14)$$

and from (9)

$$-2(C \text{ solid}) + 2f(CO_2) - 4f(CO) = 76 \cdot 8 ;$$

therefore

$$6(H) + 6f(CH) + f(C \cdot C) + 2f(CO_2) - 4f(CO) = 104 \cdot 2 = 6r + v_1. \quad ($$

So for acetylene,

$$2(C \text{ solid}) + 2(H) + f(C : C) + 2f(CH) = -47 \cdot 8, \quad . \quad (16)$$
$$-2(C \text{ solid}) + 2f(CO_2) - 4f(CO) = 76 \cdot 8 ;$$

therefore

$$2(H) + f(C : C) + 2f(CH) + 2f(CO_2) - 4f(CO) = 29 = 2r + v_3. \quad (17)$$

Thus strictly

$$r = (H) + f(CH) + \tfrac{1}{4}\{f(CO_2) - 2f(CO)\} = 15, \quad . \quad (18)$$

$$v_1 = f(C \cdot C) + \tfrac{1}{2}\{f(CO_2) - 2f(CO)\} = 14, \quad . \quad (19)$$

$$\text{from (7) } v_2 = f(C : C) + \{f(CO_2) - 2f(CO)\} = 14 \cdot 2, \quad (20)$$

$$v_3 = f(C : C) + \tfrac{3}{2}\{f(CO_2) - 2f(CO)\} = 0. \quad . \quad (21)$$

With the assumptions $f(CO_2) = 2f(CO)$, and $(H) = 0$, these simplify to :—

$$r = f(CH) = 15, . \quad . \quad . \quad . \quad . \quad . \quad (22)$$

$$v_1 = f(C \cdot C) = 14, . \quad . \quad . \quad . \quad . \quad (23)$$

$$v_2 = f(C : C) = 14 \cdot 2, \quad . \quad . \quad . \quad . \quad (24)$$

$$v_3 = f(C : C) = 0, \quad . \quad . \quad . \quad . \quad (25)$$

to which we may add (C solid)$= -38{\cdot}4$. This negative value of (C solid) is well worth notice ; if we wished to get (C), that is the value of that part of the heat-effect of a gramme-atom of gaseous carbon passing into combination which is independent of the elements it is combining with, we must add the latent heat of vaporization of a gramme-atom of carbon.

If carbon behaved like a metal, then, according to Table I *a.* of the Introduction, the latent heat of a gramme-atom of carbon would be 32, but in Part I. we multiplied the values given by Table I *a.* by $1{\cdot}6$, so that in harmony with the latent heats adopted for the metals in Part I. we should take the latent heat of the carbon gramme-atom as $51{\cdot}2$. This, therefore, gives a good general explanation for the large negative value of (C solid) ; if $51{\cdot}2$ is added on for latent heat, then (C) becomes positive with a value 13. From the latent heat and density of a metal its melting-point can be calculated by equation (11), but in the case of carbon the fact that the specific heat does not approach a value satisfying Dulong and Petit's law till near a temperature of 1000° C. precludes our getting a likely value of the melting-point for carbon from these equations ; but if amorphous carbon, with a density $2{\cdot}4$, behaved as a metal the value 32 for latent heat in equation (11) of the Introduction would give a melting-point 1535° absolute ; this is much too low, and suggests that the value adopted for the latent heat of carbon is at any rate not too large. In a general way therefore our value $-38{\cdot}4$ for (C solid) is shown to be in accordance with a general scheme of facts, and there is a probability of our not being far from the truth when we put (C)$=13$.

Some chemists have objected to the possibility of Thomsen's values $v_1 = v_2 = 14$, and $v_3 = 0$, and have implied that the equation $v_1 = v_2$ would abolish all distinction between single and double binding, and that the equation $v_3 = 0$ is tantamount to the assertion that such a thing as a triple binding does not exist. It is obvious that these objections are quite unsound, because we know it to be possible that two different configurations of the same physical system may have the same amounts of energy. One of the main objects of the study of thermo-chemistry is to discover what we call a bond really is, not to dictate on *à priori* grounds what it should be. Thomsen himself inferred from the equation $v_1 = v_2$ that so-called double bindings are only single bindings, and that compounds involving them ought to be regarded as unsaturated (in the strict sense of the term).

Having determined the fundamental constants given above, Thomsen proceeds to discuss the heat of formation of the

different types of compound included in his data, for as we know the thermal effect due to the addition of CH_2, we need only discuss the types from which all the homologous series are derived by additions of CH_2.

HEAT OF FORMATION OF TYPICAL COMPOUNDS.

1. *Hydrocarbons.*—The general formula for these is C_aH_{2b}, and it is to be remembered that Thomsen adds $a \times 38 \cdot 4$ to the heat of formation of C_aH_{2b} from amorphous solid carbon, which he denotes by p, the sum being denoted by $p + ad$, and then he writes :—

$$p + ad = 2br + \Sigma v = b30 + n14 \cdot 2,$$

where Σv stands for the sum of the thermal values of all the bindings between the carbon atoms, n being the number of single and double bindings. In our notation we have

$$p + ad = H(C_a \text{ solid}, H_{2b}) - a(C \text{ solid}) = H(C_a, H_{2b}) - a(C)$$

$$= 2bf(CH) + \Sigma f(CC). \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (26)$$

When the heat of formation of a hydrocarbon is known this equation enables us to determine the total number of single and double bindings in the molecule, and in this way it is competent to throw light on the constitution of the molecule. It happened rather unfortunately that Thomsen chose benzene as a good subject on which to illustrate the help that the thermochemical equation can give in determining the constitution of a molecule, arriving at the conclusion that the six carbon atoms of the benzene molecule must be joined by nine single bonds represented by the sides and diagonals of a hexagon ; because Stohmann was able to point out that his own and Berthelot's values for the heat of combustion of benzene agreed in being less than Thomsen's by some 12 kcal., so that the heat of formation p, and therefore $p + ad$, should be greater by 12 than they were taken to be by Thomsen ; but 12 is nearly the 14 which Thomsen takes as the value of a single and double binding, so that his system of nine bindings is possibly in error by the value of one binding; but at a later date Thomsen, in discussing some data of Stohmann for the benzene, naphthalene, and anthracene groups, treats the benzene nucleus on the Kekulé plan, that is with three double bindings and three single, and of course has to assign a larger value to the double binding in aromatic bodies than in aliphatic : but it seems to me to be undesirable first to force the bonds phraseology upon thermochemistry and

then to abandon it by giving a bond two meanings. The better course for the present seems to me to be to determine as carefully as possible the values belonging to all the nuclei for which Stohmann has been supplying a fine store of experimental determinations, and if no rational relationship between structure and thermal value in the different nuclei is discoverable, to let the matter rest at giving the thermal value for each nucleus until the rational relationship is discovered.

2. *Haloid Compounds.*—The data relate to 15 chlorine compounds, five bromine, and two iodine, from which Thomsen draws the conclusion that for a difference in composition $Br - Cl$ there is a difference in heat of formation amounting to 7·5, while for $Cl - I$ the difference is 19·4, the ratio of which is 2·6, which is identical with our mean value in inorganic compounds. But it is possible that there is some experimental error involved in this value, because Thomsen finds that the thermal value corresponding to the difference $Cl - H$ increases with the increasing molecular weight of the hydrocarbon in which the substitution of Cl for H takes place, so that in the haloid compounds in his values of $p + ad$ he is forced to represent the thermal value of CH_2, namely $v_1 + 2r$, by $13·96 + 31·44$ in place of $14·2 + 30·0$. This would be a very interesting result if it could be relied on as true, for it would demonstrate an influence exerted by an atom of halogen on every CH_2 group of the organic radical with which it is associated, and the same action on each CH_2, no matter how many there may be ; this is so improbable that we are led to suspect strongly the existence of experimental error, especially as the experiments and numerical reductions are made more complicated by the presence of the halogen. The peculiarity of some further results with chlorine compounds is also suggestive of the intrusion of experimental error : when an atom of Cl replaces H in a hydrocarbon, then in the expression for $p + ad$ for the hydrocarbon, one r is replaced by the corresponding thermal value of the bond of union of a Cl to a C ; for a single Cl this is found to be 13·5, for two Cl, as in CH_2ClCH_2Cl, it is $2 \times 16·5$, for three Cl, as in $CHCl_3$, it is $2 \times 16·5 + 13·5$, while for four Cl, as in CCl_4, it is $2 \times 16·5 + 2 \times 13·5$. To show the uncertainty that must attach to some of these numbers let us compare two of Thomsen's values with the later determinations of Berthelot and Matignon (*Compt. Rend.* cxii.) : thus Thomsen gives :—

$$C\,(\text{amorphous}) + H + 3Cl = CHCl_3\,(\text{gas}) + 23·5,$$
$$C\,(\text{amorphous}) + 4Cl \quad = CCl_4\,(\text{gas}) + 20·4,$$
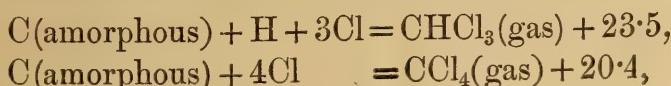
while Berthelot and Matignon's results are :—

$$C(\text{diamond}) + H + 3Cl = CHCl_3 \text{ (gas)} + 35\cdot9,$$

$$C(\text{diamond}) + 4Cl \quad = CCl_4(\text{gas}) \quad +47.$$
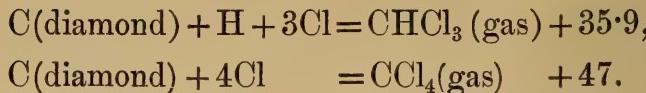
The differences in both cases ought to be the same; with Thomsen's data it is $+3\cdot1$, whereas with Berthelot and Matignon's it is $-11\cdot1$. It is quite clear that none of Thomsen's exceptional results for the haloid compounds can be accepted under such conditions of experimental uncertainty, nor can we attach much weight to his values $13\cdot4$ for the heat evolved on the junction of an atom of Cl to an atom of C, $5\cdot9$ for Br and C, and for I and C $-5\cdot9$. These are values of our $f(\text{CCl})$, $f(\text{CBr})$, and $f(\text{CI})$, and it would be of great interest to ascertain whether $f(\text{CI})$ really has a negative value : but all the essential points in the thermochemistry of the organic haloid compounds have still to be cleared up by some experimenter who can devise such means of control of his experimental results as will enable him to assign limits of error within which his results must lie. Berthelot and Matignon claim for their results for six chlorine compounds (*Compt. Rend.* cxii.) by means of explosion with compressed oxygen in presence of a sufficiency of combined hydrogen and solution of arsenious acid to prevent the formation of free chlorine, that they are the most accurate yet obtained for chlorine compounds with organic radicals. Berthelot (*Ann. de Ch. et de Ph.* 6th ser. xxviii.) finds for the evolution of heat when Cl acting on CH_4 liberates 1, 2, 3, or 4 atoms of H, the following values, $10\cdot3$, $2 \times 7\cdot1$, $3 \times 9\cdot3$, and $4 \times 12\cdot5$, whereas, according to Thomsen, these values must be all nearly zero; this shows that we can attach but little weight to Thomsen's negative value for $f(\text{CI})$, and once more proves what an excellent field for the experimental thermochemist the haloid organic compounds still remain.

3. *The Alcohols.*—The most important result is that the differences of the heats of formation of the primary alcohols and of the related paraffins are constant; that is that the heat of formation of the radical OH from gaseous oxygen and hydrogen and its substitution for an atom of H in a paraffin is constant, or, according to our notation,

$$(O) + f(\text{OH}) + f(\text{C·O}) - f(\text{CH})$$

is constant, the average value of the constant, according to Thomsen, being $29\cdot5$; and as $f(\text{CH})$ is 15, and (O) and (H) are both zero, then

$$f(\text{OH}) + f(\text{C·O}) = 44\cdot5. \quad . \quad . \quad . \quad (27)$$

Along with this we had better take the equations for gaseous H_2O and gaseous H_2O_2, namely,

$$(O) + (H) + (H) + f(OH_2) = 59, \text{ or } f(OH_2) = 59, \quad (28)$$

$$2(O) + 2(H) + 2f(OH) + f(O \cdot O) = 45, \text{ or } 2f(OH) + f(O \cdot O) = 45. \quad (29)$$

Now we ought to take $f(OH_2) = 2f(OH)$, which would give us

$$f(O \cdot O) = -14, \quad \ldots \ldots \ldots \quad (30)$$

and

$$f(OH) = 29 \cdot 5, \quad \ldots \ldots \ldots \quad (31)$$

therefore from (27)

$$f(C \cdot O) = 15. \quad \ldots \ldots \ldots \quad (32)$$

Thomsen's second result for the alcohols is that the heat of formation of a primary alcohol is less than that of the isomeric secondary and tertiary alcohols ; thus for propyl and isopropyl alcohols the difference is 5·3, for isobutyl alcohol and trimethylcarbinol it is 17·1, and for isoamyl alcohol and dimethylethylcarbinol it is 9·6. These differences are larger than those found by Louguinine (*Compt. Rend.* xci.), namely, 2 for propyl and isopropyl alcohols, and 5 for amyl alcohol and dimethylethylcarbinol. Thus the values of the differences in the heats of formation of isomeric alcohols are too irregular to encourage any further study of them at present until a better guarantee of experimental accuracy can be given.

4. *Ethers.*—In the simple and mixed oxides, as in the haloid compounds, Thomsen adopts slightly different values for his fundamental constants, namely, $v_1 = v_2 = 13 \cdot 9$ instead of 14·2, and $r = 15 \cdot 76$ instead of 15, and then, as in the ethers two carbon atoms are joined by an oxygen atom, he finds for the thermal value of such junction $2 \times 15 \cdot 76$; the reason for adopting different values for the fundamental constants is that it gives a greater uniformity amongst the values of this junction derived from the heats of formation of eight ethers in Thomsen's list ; but if the old values for v and r are retained the values of the heat of junction of an O atom to two C atoms only vary within limits which do not exceed those possible by reason of experimental error. In our symbols this $2 \times 15 \cdot 76$, which Thomsen treats as the heat of junction of two C atoms by one O, would be $f(C \cdot O \cdot C)$, and taking the old values $r = f(CH) = 15$, $f(C \cdot C) = f(C : C) = 14 \cdot 2$ we get for $f(C \cdot O \cdot C)$ the following values :—in dimethyl ether 35, in methylethyl ether 37·7, in diethyl ether 43·2, in methylpropargyl ether 37·3, in methylallyl ether 37·8, in diallyl ether

34·6, and in methylphenyl ether 37·7, or, on the average, about 37 : thus we add another to our list of functions, namely,

$$f(C \cdot O \cdot C) = 37. \quad . \quad . \quad . \quad . \quad . \quad . \quad (33)$$

But $f(C \cdot O \cdot C)$ should equal $2f(C \cdot O)$, and therefore in the ethers $f(C \cdot O) = 18 \cdot 5$ in conflict with the 15 of (32) from the alcohols H_2O and H_2O_2 ; the difference is probably due to secondary influences of unconnected atoms on one another, and these are neglected in the present discussion.

In the case of ethylene oxide CH_2OCH_2, for which $p + ad$ is 94, Thomsen argues that with the value 15·76 for r and $2 \times 15 \cdot 76$ for the junction of O to two C atoms, the $4r$ and this $2 \times 15 \cdot 76$ or 94·54 account for the whole of $p + ad$, namely 94, and urges therefore that the two CH_2 groups cannot be united by a single binding according to the accepted structure of CH_2OCH_2, for that would introduce an additional 13·9 for the thermal value of this binding and would give a result discordant with experiment. According to Thomsen, then, CH_2OCH_2 must be supposed to involve in its structure no direct connexion of the one CH_2 with the other, and it must therefore be a genuinely unsaturated compound. But in connexion with the general chemistry of CH_2OCH_2 it seems better to take $94 - 60$ or 34 as the value of $f\left(\begin{smallmatrix} CC \\ O \end{smallmatrix}\right)$, the arrange-ment $\begin{smallmatrix} CC \\ O \end{smallmatrix}$ denoting the ring (or triangular) connexion of the atoms, and to wait for more knowledge of the thermochemistry of ring nuclei before attempting to interpret the fact that $f\left(\begin{smallmatrix} CC \\ O \end{smallmatrix}\right)$ is actually less than $f(C \cdot O \cdot C)$.

5. *Aldehydes, Ketones, Acids, and Anhydrides.*—When the formula for an aldehyde $C_aH_{2a}O$ is written in the form $C_{a-1}H_{2a-1}COH$ we can write for $p + ad$ the equation

$$p + ad = (a-1)v_1 + (2a-1)r + q,$$

where q is the heat developed in the attaching of H and O to C in the aldehyde group COH ; from the heats of formation of acetic, propionic, and butyric aldehydes Thomsen gets for q the mean value 65·4. In a ketone $C_aH_{2a+1}COC_\beta H_{2\beta+1}$ or $C_aH_{2a}O$ we have $p + ad = (a-1)v_1 + 2ar + s$, where s is the heat of junction of O to C to produce the CO characteristic of the ketones ; from dimethyl and methylpropyl ketones the mean value found for s is 54·2.

Again, in the acids $C_{a-1}H_{2a-1}COOH$ we have the equation $p + ad = (a-1)v_1 + (2a-1) \, r + t$, where t is the heat of attach-

ment of O to C plus the heat of formation of OH and of its attachment to C to produce the COOH characteristic of acids ; and from formic, acetic, and propionic acids the mean value derived for t is 120. As $q + s = 119\cdot6$, Thomsen writes $q + s = t$, and proceeds from this equation to deduce a heterodox structure for the aldehydes ; first, he assumes the ordinary structures of the ketones and acids, namely, those denoted above by their general formulæ, that is, that COOH in the acids is of the form $O:\overset{..}{C}\cdot OH$, and CO in the ketones of the form $O:C:$, then it follows from the equation $q + s = t$ that in the COH of the aldehydes the O and H must be united as hydroxyl HO, and the $\overset{.}{C}$ must have two unsaturated bonds ; thus in place of the usual form $O : \overset{.}{C} \cdot H$ Thomsen declares for $HO \cdot \overset{.}{C} :$. Before discussing these results in our notation we may as well take the related results for the esters.

6. *Esters.*—A difficulty arises in connexion with the values of $p + ad$ for the esters, because for the three isomers, propyl formate, methyl propionate, and ethyl acetate, Thomsen obtains the three values $253\cdot7$, $258\cdot5$, and $265\cdot9$, although to be in harmony with the general principles holding for most of the carbon compounds these ought to be more nearly equal. As Thomsen took special pains to check the value for ethyl acetate he considered that as the value for propyl formate takes its right place in the series for the esters, the discrepant value for ethyl acetate points to the fact that ethyl acetate has a structure quite different from that usually assigned, namely, that it contains the hydroxyl group, in short that it is $CH_3\cdot CH(OH)\cdot CO\cdot CH_3$ instead of $CH_3\cdot COOC_2H_5$. A piece of heterodoxy like this has naturally made many chemists dubious about the value of all Thomsen's analysis of thermochemical data.

From the data for methyl formate, methyl acetate, ethyl formate, propyl formate, and methyl isobutyrate it appears that the fixing of the two atoms of O in the molecule is accompanied by the evolution of $105\cdot4$ kcal. For dimethyl carbonate and diethyl carbonate the values of $p + ad$ are $251\cdot5$ and $341\cdot2$, whence, for the fixing of the three atoms of O in their molecules, we find a mean evolution of $162\cdot1$ kcal. We can now state and discuss altogether in our notation these relations for the aldehydes, ketones, acids, anhydrides, and esters. But in the case of the acids we must first introduce a correction for the polymerization that has been proved to be associated with their abnormal vapour densities. According to the measurements of Berthelot and Ogier (*Ann. de Ch. et de Ph.* 5th ser. xxx.) the heat required to dissociate a

gramme-molecule (60 grammes) of acetic acid from its state at the ordinary boiling-point into the monomolecular state is 4·8 kcal., so that from the heats of formation of the acids, as given by Thomsen, we must subtract about 5 kcal. to get the heats of formation of the monomolecular acids and thus his value for t, namely 120, must be reduced to 115.   In our notation we have the following relations :—

In the aldehydes,

$$f(C:O)+f(CH)=65·4, \quad \therefore f(C:O)=50·4 ; . \quad (34)$$

in the ketones,

$$f(C:O)=54·2 ; . . . . (35)$$

in the acids,

$$f(C:O)+f(C \cdot O)+f(OH)=115 ; . . . . (36)$$

in the esters,

$$f(C:O)+f(C \cdot O \cdot C)=105 ; . . . . (37)$$

in the anhydrides,

$$2f(C:O)+f(C \cdot O \cdot C)=165·9; . . . . (38)$$

in the carbonates,

$$f(C:O)+2f(C \cdot O \cdot C)=162·1. \quad . . . . (39)$$

From the last two equations it would appear that $f(C:O)$ and $f(C \cdot O \cdot C)$ must be nearly equal and have each a value about 54, but in (33) with the ethers we found for $f(C \cdot O \cdot C)$ the value 37, which is in conflict with that just found.   This conflict is due to (39), which for the present we will exclude from consideration.

Using in (36) the value for $f(C \cdot O)+f(OH)$ given by (27) in the alcohols, namely 44·5, and using in (37) and (38) the value 37 for $f(C \cdot O \cdot C)$ given by (33) for the ethers, we get the following list of values for $f(C:O)$, namely 50·4 in the aldehydes, 54·2 in the ketones, 70·5 in the acids, 68 in the esters, 64·4 in the anhydrides, and if we now take account of (39) it is 88·1 in the carbonates ; these cluster about the following three mean values, namely, 52 in the aldehydes and ketones, 68 in the acids, esters, and anhydrides, and 88 in the carbonates.   Now if we denote the junction of the O of OH to C in the characteristic acid group COOH by the symbol (C·O acid) then the equations (34) to (39) become:— in the aldehydes,

$$f(C:O)=50·4 ;$$

in the ketones,

$$f(C:O)=54·2 ;$$

in the acids,

$$f(C:O) + f(C \cdot O \text{ acid}) + f(OH) = 115 ; \quad (39\,a)$$

in the esters,

$$f(C:O) + f(C \cdot O \cdot \text{acid } C) = 105 ; \quad . \quad . \quad (40)$$

in the anhydrides,

$$2f(C:O) + f(C \cdot O \cdot \text{acid } C) = 165 \cdot 9 ; \quad . \quad (41)$$

in the carbonates,

$$f(C:O) + 2f(C \cdot O \cdot \text{acid } C) = 162 \cdot 1. \quad . \quad . \quad (42)$$

It can be seen that the reason for the occurrence of the three mean values given above for $f(C:O)$ is, that in the equations for the aldehydes and ketones the term $f(C \cdot O \text{ acid})$ occurs no times, in the equations for the acids, esters, and anhydrides occurs once, and in the equation for the carbonates twice ; so that if, instead of taking $f(C \cdot O \text{ acid})$ and $f(C \cdot O \cdot \text{acid } C)$ to be the same as $f(C \cdot O)$ and $f(C \cdot O \cdot C)$ in the alcohols and ethers, as we did in solving the equations (34) to (39), we assume $f(C \cdot O \text{ acid}) = f(C \cdot O) + 15$ and $f(C \cdot O \cdot \text{acid } C) = f(C \cdot O \cdot C) + 15$, then the three values found above for $f(C:O)$ would become 52 in the aldehydes and ketones, 53 in the acids, esters, and anhydrides, and 58 in the carbonates.

This difference between $f(C \cdot O)$ and $f(C \cdot O \text{ acid})$ appears as the first pronounced exception to our fundamental hypothesis that the heat evolved on the junction of two atoms depends only on the two atoms, and not on the other atoms with which either may be associated. In the case of the junction denoted by $(C \cdot O \text{ acid})$ the most characteristic feature is that the C atom is joined by two bonds to another O atom—that is, $f(C \cdot O \text{ acid})$ is always associated with $f(C:O)$; and this association produces an increase of thermal effect amounting to 15. Thus we have a case of atoms affecting one another without being directly connected ; and it is interesting to find this phenomenon occurring in connexion with the profound distinction that exists between the hydroxyl of acids and the hydroxyl of alcohols.

We can see that the difference between the $50 \cdot 4$ for $f(C:O)$ in the aldehydes and the $54 \cdot 2$ in the ketones is not sufficient to warrant the peculiar change of constitution suggested by Thomsen for the aldehydes.

Returning to the value for $f(C:O)$, which we have found to be about 53, let us consider again our early assumption $(7\,a)$ that $f(CO_2) = 2f(CO) = 135 \cdot 3$. Now $f(CO_2) = 2f(C\overset{\text{iv}}{:}O)$, marking the tetrad character of the carbon, while in carbonic oxide

the C atom is dyad. In carbonic dioxide each junction C^{iv}:O is associated with the other junction C^{iv}:O; and according to what we have just seen this association ought probably to be characterized by an evolution of 15 kcal.; so that for $f(C^{iv}O)$, free from the effect of associated oxygen, we get the value $135\cdot3/2-15$ or $52\cdot6$ in harmony with the values found in organic compounds; and then comparing the values $67\cdot6$ for $f(C^{ii}O)$ in carbonic oxide, and $52\cdot6$ for $f(C^{iv}O)$, we see the passage from tetrad to dyad carbon is accompanied by an evolution of 15 kcal. per gramme-atom. Now if in the bonds phraseology we say that the conversion of tetrad to dyad carbon is due to two bonds of the same atom satisfying one another, then the heat of formation of dyad from tetrad carbon would be $f(C\cdot C)$, which in CO we have just found to be 15, and which as one of the fundamental constants for organic compounds we found to be 14, which is nearly the same. Thus, then, the thermochemistry of the oxides of carbon and of the alcohols, ethers, aldehydes, ketones, acids, esters, and anhydrides can to a first approximation be brought into consistency by the system of values $f(C\cdot C)=f(C:C)=14\cdot2$, $f(CH)=15$, $f(C\cdot O\cdot C)=2f(C\cdot O)=37$, $f(C\cdot O)+f(OH)=44\cdot5$, $f(C:O)=53$, with the provisos that the association of the junctions C:O and C·O, or C:O and C:O, is accompanied by the evolution of 15 kcal. for each C:O, and that the conversion of tetrad into dyad carbon is accompanied by an evolution of heat 15, or nearly $f(C\cdot C)$.

7. *Nitrogen in Organic Compounds.*—In treating of the thermochemistry of nitrogen, Thomsen starts by seeking for the thermal value of the bond uniting two N atoms. He

assumes that nitrogen dioxide has the constitution $N{\displaystyle<}{\textstyle{O \atop O}}$, and nitric peroxide ${\textstyle{O \atop O}}{\displaystyle>}N{-}N{\displaystyle<}{\textstyle{O \atop O}}$; so that the heat evolved when two molecules of NO_2 unite to form one of N_2O_4 is the required thermal value of a single binding between two nitrogen atoms. Now from Berthelot's and Ogier's measurements of the specific heat of gaseous N_2O_4, as with rising temperature it gets dissociated into $2NO_2$ (*Ann. de Chim. et de Phys.* 5th ser. xxx.), it follows that the heat required for the complete dissociation is $13\cdot25$, while a theoretical estimate made by Boltzmann on thermodynamical grounds gave the value $13\cdot9$. Thomsen takes the mean $13\cdot6$, and subtracting $\cdot6$ for the doubling of the volume, gets 13 as the heat of complete dissociation of N_2O_4 at constant volume, and this, then, he takes as the thermal value of a single binding of two N atoms.

The heat of formation of pure N_2O_4 at 18° C. is given by Thomsen as -3.8, so that the heat of formation of NO_2 is -8.4. It will be noticed that Thomsen has made quite an arbitrary assumption as to the constitution of NO_2, which could be $O=N=O$ rather more reasonably than $N\!\!<\!\!\begin{smallmatrix}O\\[2pt] \;\,\mid\\[2pt] O\end{smallmatrix}$; and in his further treatment of the oxides of nitrogen, assumptions become more abundant than facts. Thus he assumes that, because in the case of carbon $v_1 = v_2$, or $f(C \cdot C) = f(C : C)$, therefore it is likely that the single binding of the two O atoms in his assumed constitution of NO_2 is the same in thermal value as the binding of two O atoms to form the O molecule ; and accordingly the heat of formation of $2NO_2$, namely -16.8, is four times the thermal value of a single binding between N and O, minus the heat required to break the N molecule into two N atoms, namely 13. Thus the thermal value of a single binding between N and O is obtained as $-.95$; or, as this is small, it is taken as zero by Thomsen. Turning now to nitrogen monoxide NO, the heat of formation of which is -21.6, Thomsen assumes that the double binding between O and N which its structure involves has double the thermal value of the single binding and is therefore zero, and he then deduces for the thermal value of a single binding between two oxygen atoms the value 26.3.

It is evident that a satisfactory investigation of the oxides of nitrogen is not easy, and the accumulated assumptions in Thomsen's attempt being untested in any cases beyond those which they were first devised to meet remain pure assumptions. He does not apply them to the interesting cases of N_2O and N_2O_5, where they fail unless supported by still further assumptions. For on Thomsen's principles the structure of N_2O ought to be taken either as $N{-}O{-}N$ or $N\!\!\stackrel{O}{=}\!\!N$; according to the first of which the heat of formation would be $2 \times 0 - 13 - \frac{1}{2} \times 26.3$ or -26 ; and according to the second, $2 \times 0 - \frac{1}{2} \times 26.3$, or -13, while the experimental number is -18. Again, according to Thomsen, the structure of N_2O_5 would probably be $\begin{smallmatrix}O\\[-2pt]\diagdown\end{smallmatrix}N{-}O{-}N\begin{smallmatrix}\diagup O\\[-2pt]\diagdown\,O\end{smallmatrix}$, the heat of formation of which, according to his values, ought to be $6 \times 0 - \frac{1}{2} \times 26.3 - 13$, or -26, whereas the experimental number is zero. The structure $\begin{smallmatrix}O=\\O=\end{smallmatrix}N{-}O{-}N\begin{smallmatrix}=O\\=O\end{smallmatrix}$ would give the value

$$10 \times 0 - 13 - \tfrac{5}{2} \times 26.3,$$

or -78, which is still worse.   This case is decisive as to the purely arbitrary character of Thomsen's analysis of the thermochemistry of the oxides of nitrogen : nor can a less arbitrary interpretation be given to that analysis, and in searching for a more reasonable idea of the thermochemical relationship of these compounds we must start afresh.

The chief difficulty with the oxides of nitrogen is, that we have so little general chemical knowledge of their constitution on account of the pentad and triad nature of the N atom and the unsaturated state of some of them.   But let us make a scheme of the simplest available structural formulæ on the supposition that N is always pentad.

$$\begin{matrix} O= \\ O= \end{matrix} N{-}O{-}N{\begin{matrix} =O \\ =O \end{matrix}}, \quad \begin{matrix} O= \\ O= \end{matrix}N{-}N{\begin{matrix} =O \\ =O \end{matrix}}, \quad -N{\begin{matrix} =O \\ =O \end{matrix}}, \quad {\equiv}N{=}O, \quad \begin{matrix} N{\equiv}N \\ \diagdown \ \diagup \\ O \end{matrix}$$
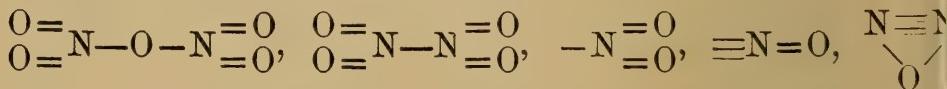
The first two are saturated, the next two are unsaturated, and the last may be saturated, though not necessarily so.   Let us next write in the same order the heats of formation

$$0 \qquad -3{\cdot}8 \qquad -8{\cdot}4 \qquad -21{\cdot}6 \qquad -18$$

It will be noticed that although N_2O_5 and N_2O_4 involve more than twice as many molecules in their construction as NO_2 and NO, the numerical values of their heats of formation are much smaller.   If for the saturated compounds N_2O_5 and N_2O_4 we write in our notation the equations for the heat of formation with the assumption $(N)=0$, to go along with $(O)=0$, $(Cl)=0$ and so on, we get

$$4f(N{:}O) + 2f(N{\cdot}O)=0, \quad . \ . \ . \ . \ . \ (43)$$
$$4f(N{:}O) + f(N{\cdot}N) = -3{\cdot}8 ; \quad . \ . \ . \ . \ (44)$$

from which we are entitled to infer that $f(N{:}O)$, $f(N{\cdot}O)$, $f(N{\cdot}N)$, are all small, as it is unlikely that $f(N{:}O)$ and $f(N{\cdot}O)$ will have opposite signs.   If then we can put $f(N{:}O)=f(N{\cdot}O)=0$, then the $-8{\cdot}4$ for the formation of NO_2 represents the thermal effect of the passage of the N atom from the N molecule to the pentad combined state with one bond unsaturated, and the $-21{\cdot}6$ for NO represents the thermal effect for the passage of the N atom from the N molecule to the combined state, with, perhaps, three bonds unsatisfied.   In the case of N_2O we can hardly suppose an unsaturated structure to account for the -18, perhaps we have to do with a ring structure such as is indicated above, and has no simple relation to the other structures under consideration.   From the present point of view then, the numerically larger negative heats of formation of NO_2 and NO as compared with those of N_2O_5 and N_2O_4 are regarded as due to the unsaturated state of the N atom in them.

8. *Cyanides.*--The heats of formation of hydrocyanic acid, acetonitrile, and propionitrile from solid amorphous carbon are $-27\cdot6$, $-16\cdot3$, and $-10\cdot8$, so that the values of $p+ad$ are $10\cdot9$, $60\cdot5$, and $104\cdot3$, the differences between which are $49\cdot6$ and $43\cdot8$, the latter is practically equal to the $44\cdot2$ due to CH_2 in homologous series, but the former $49\cdot6$ is larger by $5\cdot4$ kcal., on the strength of which Thomsen proposes for HCN an entirely different constitution from that of the cyanides; thus he treats acetonitrile as $H_3C\cdot C:N$ and propionitrile as $H_5C_2\cdot C:N$, but hydrocyanic acid as $H\cdot C\cdot N$, and then he assigns the thermal values of the junctions $C:N$ and $C\cdot N$ as $7\cdot6$ and $2\cdot4$. For cyanogen C_2N_2 the heat of formation is $-65\cdot7$, and $p+ad=11\cdot1$, on account of which Thomsen assigns to it the structure $C:N\cdot N:C$, and obtains for the thermal value of the junction $C:N$ $5\cdot5$; and he points out that the values of the three junctions $C\cdot N$, $C:N$, $C:N$ are as 1, 2, and 3. But it is obvious that the structures for HCN and C_2N_2 are assigned in a manner relating only to thermochemical, and not to general chemical considerations, whereas we should be guided in the converse manner and establish the foundations of the thermochemical theory in accordance with established chemical law.

Let us then try to express in our notation the pure facts relating to cyanogen and the cyanides: if there is need for distinction between pentad and triad N let its thermal effect be α; for the values of $p+ad$ for acetonitrile and propionitrile we have the expressions

$$3f(CH) +\ f(C\cdot C)+f(C:N)+\alpha=60\cdot5, \quad . \quad . \quad (45)$$

$$5f(CH) +2f(C\cdot C)+f(C:N)+\alpha=104\cdot3, \quad . \quad . \quad (46)$$

in which using the values $f(CH)=15$, $f(C\cdot C)=14\cdot2$, we get $f(C:N)+\alpha=1\cdot3$ in acetonitrile, and $\cdot9$ in propionitrile, or $1\cdot1$ in the mean. Now if we proceed with the value for HCN in the same way we get $f(CH)+f(C:N)+\alpha=10\cdot9$, whence $f(C:N)+\alpha=-4\cdot1$. The reason for the discrepancy in these two values of $f(C:N)+\alpha$ is not hard to find, for in HCN we have taken the thermal value of the junction CH to be the same as it is in CH_4, although the association of the N with the C has conferred on the H the character of the H in acids; thus, then, we have to do with another case of a mutual influence of atoms that are not directly connected. In most cases we have been able to neglect these mutual influences in our first approximations, but the amount of it here, namely $5\cdot2$ kcal., shows the importance of proceeding to second approximations as soon as the data permit of making the attempt. It can be seen that there is no need to accept

Thomsen's structure for HCN. Our equation for cyanogen is :—

$$f(\mathrm{C \cdot C}) + 2\,f(\mathrm{C:N}) + 2\alpha = 11\cdot1, \quad . \quad . \quad . \quad . \quad (47)$$

$$\therefore\; 2\,f(\mathrm{C:N}) + 2\alpha = -3\cdot1, \quad \therefore\; f(\mathrm{C:N}) + \alpha = -1\cdot5.$$

Here we have another value for $f(\mathrm{C:N}) + \alpha$, showing again evidence of a subsidiary action, but perhaps the experimental error does not allow of a very definite measure of it. To a first approximation then we can write

$$f(\mathrm{C:N}) + \alpha = 0. \quad . \quad . \quad . \quad . \quad . \quad (48)$$

9. *Amines.*—In the values of $p + ad$ for the amines, Thomsen finds the effect of CH_2 rather larger than the $44\cdot2$ taken as the normal amount of it, and in this respect the amines agree with the halogen compounds and the oxides, but it is probable that slight experimental error is responsible in all these cases for the slight excess in the value for CH_2. The values of $p + ad$ for a monamine and the isomeric diamine and triamine are not equal, nor should they be expected to be so, seeing that these are not strict isomers, as their structure involves the displacement of one, two, and three atoms of H from ammonia. The thermal effect of these displacements is the most important point in the thermochemistry of the amines, and is shown in the column of differences in the following table of values of $p + ad$:—

		Diff.				Diff.
NH_3	11·3			NH_3	11·3	
		35·5				81·2
CH_3NH	46·8			$C_2H_5NH_2$	92·5	
		41·0				87·4
$(CH_3)_2NH$	87·7			$(C_2H_5)_2NH$	179·9	
		41·0				88·3
$(CH_3)_3N$	128·7			$(C_2H_5)_3N$	268·3	

The first substitution of CH_3 for H in NH_3 seems to be accompanied by a smaller thermal effect than the second and third, and on account of this fact and the values which he has already assigned to the junctions, Thomsen proposes for the mono-, di-, and tri-methyl amines the peculiar constitutions

$$H_2C:NH_3, \qquad \begin{matrix} H_2C \\ \\ H_3C \end{matrix}\!\!\diagdown\!\!\diagup NH_2, \;\; \text{and} \;\; \begin{matrix} H_2C \\ \\ H_3C \end{matrix}\!\!\diagdown\!\!\diagup H_3C\!-\!NH.$$ From our point of
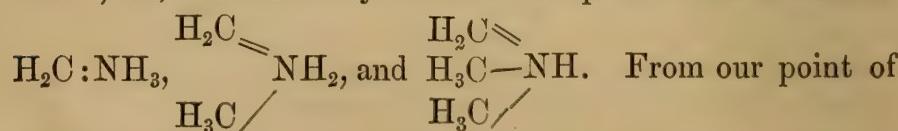
view the difference between the first and the second and third substitutions of CH_3 for H in ammonia is due to the mutual effect of unconnected atoms to be investigated in the second

approximations. In a first approximation we will neglect the difference, and determine a mean thermal value for the substitution. If in the series of differences given above for the ethylamines we subtract 44·2 as due to CH_2, then we get for the formation and substitution of CH_3 for H in NH_3 from the ethylamines the values 37·0, 43·2, and 44·1, which with the three values from the methylamines give a mean value of 40. With the usually accepted constitution for the amines and our notation, we have

$$f(C \cdot N) + 3f(CH) - f(NH) = 40, \quad \ldots \quad \ldots \quad (49)$$

$$\therefore \ f(C \cdot N) - f(NH) = -5;$$

but $\alpha + f(NH_3) = 11 \cdot 3,$

$$\therefore \ f(NH) = 3 \cdot 8 - \frac{\alpha}{3}, \quad \ldots \quad \ldots \quad \ldots \quad (50)$$

$$\therefore \ f(C \cdot N) = -1 \cdot 2 + \frac{\alpha}{3} \quad \ldots \quad \ldots \quad \ldots \quad (51)$$

This value for $f(C \cdot N)$ found from the amines should be compared with those found for $f(C : N) + \alpha$, namely 1·1 in the nitriles, $-4 \cdot 1$ in HCN, and $-1 \cdot 5$ in C_2N_2. It seems as though $f(C \cdot N)$, $f(C : N)$, and α are so small as to be each practically zero. Now the fact that there is little or no thermal difference between pentad and triad N need not surprise us, for in triad N we can imagine 2 of the 5 bonds to satisfy one another; in the case of C this appeared to be accompanied with a thermal effect $f(C \cdot C)$, so that in that of N the effect would be $f(N \cdot N)$ which we have already inferred to be zero. The case of triad N is very different from that of unsaturated N in NO_2 and NO, where an odd number of bonds are left unsatisfied in any way.

In the region of first approximations this is about all that we can get from the data for the amines, and there is no encouragement at present to go into the minor points in Thomsen's data until we know what are the limits of experimental error in the heats of formation of the amines, for there is no certainty whether a minor phenomenon is a genuine one in thermochemistry or a relatively small error in a heat of combustion which has become a relatively large one in a heat of formation. Nor would there be any profit in discussing the case of aniline in view of the uncertainty about Thomsen's numbers for benzene, and the thermochemistry of pyridine can hardly be discussed apart from that of the benzene nucleus.

10. *Nitro-Compounds.*—The values of $p+ad$ for nitro-methane and nitroethane are 55·8 and 101·9, from which Thomsen subtracts $3\,r$ and $5\,r+v_1$ respectively, having as mean remainder 11·8 for the heat of forming the group NO_2, and attaching it to a carbon atom in the CH_3 or C_2H_5, but for the junction of C and N by a single bond Thomsen takes his former value 2·6, so that 9·2 remains for the heat of formation of NO_2, but according to experiment this heat of formation is really $-8·4$; and Thomsen concludes from this discrepancy that the nitroparaffins cannot contain the group NO_2, proceeding to show that according to his thermochemical constants the nitroparaffins must be regarded as paraffins in which two atoms of H are replaced by the two groups NO and OH.

But we shall see immediately that there is no necessity to assign this improbable constitution to the nitroparaffins, for, accepting the orthodox constitution such as $H_3C-N{=O \atop =O}$, we have in our notation the equation

$$f(C \cdot N) + 2f(N:O) = 11·8; \quad \ldots \quad (52)$$

but in our study of the oxides we gathered that $f(N:O)$ is small and might be taken as zero, and in the amines $f(C \cdot N)$ was seen to be probably small, say zero : thus equation (52) discloses a secondary effect which will be discussed in connexion with another to which we proceed.

For the nitrites of ethyl, isobutyl, and amyl, Thomsen gives the following values of $p+ad$, namely, 105·6, 198·4, and 236·6; but for the formation of ethyl, isobutyl, and amyl we have the expressions $5r+v_1$, $9r+3v_1$, and $11r+4v_1$, whose values are 89·2, 177·6, and 221·8 : so that for the formation of the $-O-N=O$ and its attachment to the free carbon bond of the alkyl radicals we have the values 16·4, 20·8, and 14·8, of which the mean is 17·3, whence the equation

$$. f(C \cdot O) + f(N \cdot O) + f(N:O) = 17·3, \quad . \quad . \quad (53)$$

$$\therefore \quad f(C \cdot O) = 17·3, \quad . \quad . \quad . \quad . \quad (54)$$

a result in harmony with the values 18·5 and 15 formerly found, see (33).

Now for ethyl nitrate the value of $p+ad$ is 115·5 ; subtracting 89·2 for ethyl, we get for the formation of $-O-N{=O \atop =O}$ and its attachment to ethyl the value 26·3, whence the equation

$$f(C \cdot O) + f(N \cdot O) + 2f(N:O) = 26·3, \quad . \quad . \quad (55)$$

and therefore $f(C \cdot O) = 26 \cdot 3$,

which is larger by 9 than the value just found in (54), just another such discrepancy as we found above in (52). To try to understand this, let us reproduce side by side equations (51) (52) (53) and (55) and (43) :—

In the amines with triad N,

$$f(C \cdot N) = 0 \text{ nearly ;}$$

in the nitroparaffins with pentad N,

$$f(C \cdot N) + 2 f(N:O) = 11 \cdot 8 ;$$

in the nitrites with triad N,

$$f(C \cdot O) + f(N \cdot O) + f(N:O) = 17 \cdot 3 ;$$

in the nitrates with pentad N,

$$f(C \cdot O) + f(N \cdot O) + 2 f(N : O) = 26 \cdot 3 ;$$

in N_2O_5 with pentad N,

$$2 f(N \cdot O) + 4 f(N:O) = 0.$$

If we remember that $f(C \cdot O)$ is about $18 \cdot 5$, we see that the one consideration which will harmonize the five equations is that the introduction of a second $N : O$ binding into an N atom connected with C or with O connected with C, is attended by an evolution of about 10 kcal. Whether this, besides harmonizing the five equations, is a true phenomenon would require more experimental facts to decide ; but, meanwhile, we can claim that the nitroparaffins and the nitrates agree in showing the mutual operation on one another of atoms which are not directly connected, and that there is no necessity to devise a new structure for the nitroparaffins to explain their thermochemistry, because the nitrates by the same token would also require an amended constitution, which is very improbable.

11. *Sulphur Compounds.*—Thomsen's data for the heat of formation of the sulphur compounds relate to solid rhombic sulphur : the latent heat of vaporization of a gramme-atom of sulphur, according to Berthelot's table of latent heats, is only $2 \cdot 3$ kcal.; so that it is only necessary to increase Thomsen's heats of formation by $2 \cdot 3$ per gramme-atom of sulphur to get at least approximate values for the heat of formation from gaseous sulphur. In the following table are given all but two of Thomsen's data for the heats of formation p and $p + ad$ for the sulphur compounds from solid sulphur, along with values of p and $p + ad$ for gaseous sulphur :—

	SOLID S.		GASEOUS S.	
	p.	*p* + *ad.*	*p.*	*p*+*ad.*
HSH	2·7	2·7	5·0	5 0
CH₃SH	5·4	43·7	7·7	46·0
C₂H₅SH...........	13·3	90·0	15·6	92·3
(CH₃)₂S	11·6	88·3	13·9	90·6
(C₂H₅)₂S	26·2	179·7	28·5	182·0
CS₂	−25·4	12·9	−20·8	17·5
COS	37·3	75·7	39·6	78·0
CH₃SCN .... (methyl cyanate)	−32	44·8	−29·7	47·1
CH₃NCS .... (methyl sulpho-carbimide)	−25·1	51·7	−22·8	54·0

(S) if not zero is probably small, so we will for the present merge it in the symbols $f(\ )$.

Then from HSH we get

$$f(\text{SH}) = 2\cdot 5 ; \quad . \quad . \quad . \quad . \quad (56)$$

from CH₃SH

$$f(\text{C·S}) + f(\text{SH}) = 1\cdot 0,$$

from C₂H₅SH

$$f(\text{C·S}) + f(\text{SH}) = 3\cdot 1,$$

in the mean

$$f(\text{C·S}) + f(\text{SH}) = 2\cdot 0 ; \quad . \quad . \quad . \quad . \quad (57)$$

from (CH₃)₂S

$$f(\text{C·S·C}) = \ \cdot 6,$$

from (C₂H₅)₂S

$$f(\text{C·S·C}) = 3\cdot 6,$$

in the mean

$$f(\text{C·S·C}) = 2\cdot 1. \quad . \quad . \quad . \quad . \quad (58)$$

From (56) (57) and (58) it follows that $f(\text{C·S})$ is small, say zero.

From CS₂, $f(\text{CS}_2) = 17\cdot 5$, but $f(\text{CO}_2) = 135\cdot 3$;

$$\therefore \ f(\text{CO}_2) - f(\text{CS}_2) = 117\cdot 8.$$

From COS, $f(S : C : O) = 78$, but $f(CO_2) = 135 \cdot 3$,

$$\therefore f(CO_2) - f(S : C : O) = 57 \cdot 3 ;$$

so that

$$f(CO_2) - f(CS_2) = 2 \{f(CO_2) - f(S : C : O)\} \text{ nearly. } \quad (59)$$

We have introduced the corresponding data for O here because of the mutual action which we found two $C : O$ bindings to exercise, and the method of treatment of the data for CS_2 and SCO has shown that the $C : O$ and the $C : S$ bindings exercise the mean influence of two $C : S$ and two $C : O$ bindings ; for, denoting the mutual influence of two $C : S$ bindings on one another by α, of two $C : O$ by β, and a $C : S$ and a $C : O$ by γ, then we have the relations

$$2\{ f(C : O) - f(C : S) + \beta - \alpha\} = 117 \cdot 8,$$

$$f(C : O) - f(C : S) + 2\beta - 2\gamma = 57 \cdot 3,$$

and the approximate inference

$$2\{f(C : O) - f(C : S) + 2\beta - 2\gamma\} = 2\{f(C : O) - f(C : S) + \beta - \alpha\},$$

whence

$$2\gamma = \alpha + \beta = \alpha + 15.$$

Thus from the data for CS_2 and SCO we get

$$2f(C : S) + 2\alpha = 17 \cdot 5, \quad . \quad . \quad . \quad . \quad . \quad (60)$$

$$f(C : S) + f(C : O) + 2\gamma = 78 \cdot 0, \text{ but } f(C : O) = 53,$$

$$\therefore \quad f(C : S) + \alpha = 10 ; \quad . \quad . \quad . \quad . \quad . \quad (61)$$

or, in the mean from (60) and (61),

$$f(C : S) + \alpha = 9. \quad . \quad . \quad . \quad . \quad . \quad . \quad (62)$$

From methyl cyanate we get

$$f(C \cdot S \cdot C) + f(C : N) = 2 \cdot 1 ;$$

but $f(C : N) = 0$ nearly, $\therefore f(C \cdot S \cdot C) = 2 \cdot 1$ nearly—a value in good agreement with that in (58).

From methyl isocyanate or methyl sulphocarbimide we get

$$f(C \cdot N) + f(C : N) + f(C : S) = 9 \cdot 0 ; \quad . \quad . \quad (63)$$

whence, as $f(C \cdot N)$ and probably $f(C : N)$ are small, $f(C : S) = 9 \cdot 0$ nearly, which along with (62) makes α small, say zero.

The two compounds for which we have not reproduced Thomsen's data are thiophene and allyl sulphocarbimide,

because thiophene can only be considered in connexion with benzene and other ring nuclei, and allyl sulphocarbimide gives practically the same result as the methyl sulphocarbimide.

Summary of Results.

The present theoretical analysis of thermochemical data has been confined almost exclusively to those compounds whose heat of formation can be separated into parts due to the mutual actions of atoms which, according to the bond theory, are joined by bonds, the action between atoms which, though in the same molecule, are not joined by bonds being negligible in a first approximation. Thomsen showed that the great majority of organic compounds belong to this class, and his method of analysis consisted in determining the value of the various bindings in organic chemistry, a binding being a pair of bonds which are joined to one another ; and in the first part of this paper it was shown that in the haloid compounds of the metals the heats of formation are so related as to prove that the heat of formation is the sum of two parts, one depending on the metal and the other on the metal and the halogen. But there exists another class of compounds, of which the ammonium salts may be taken as a type, in which the mutual action of unconnected atoms becomes of the first importance, for the four atoms of H in NH_4Cl profoundly affect the thermal attitude of the N towards the Cl from what it is towards each Cl in NCl_3 ; but this class of cases, which is small, has not been discussed in the present inquiry. which has been, as far as possible, limited to such thermal relationships of directly connected atoms as show themselves free from large perturbations due to other atoms.

By not allowing for such perturbations Thomsen was led to assign peculiar and untenable structures to several compounds ; but when allowance is made for them and the heterodox structures are removed, the remainder of his analysis constitutes a pioneer advance into the region of thermochemical law. Thomsen's method of expressing his results was in accord with his discovery, for he assigned to each binding a thermal value. In accordance with the results for the haloid compounds of the metals I have adopted a slightly different mode of expression, and have separated the heat of formation of a compound RS into three parts, (R), (S), and $f(RS)$; of which (R) depends only on R, and (S) on S, while $f(RS)$ depends on both R and S. In the haloid compounds of the metals I was led to conclude that (Cl), (Br), and (I) are zero, while the corresponding parameters for the

metals do not vanish. By analogy it was assumed that (O) and (N) are both zero, though from a mathematical point of view it does not matter whether they are zero or not ; for in (R) + (S) + f(RS), to assume that (R) is zero is the same as merging it in f(RS). The values determined for f(RS) from Thomsen's data for organic compounds are as follows :—

f(C·C)=14. f(C:C)=14·2. f(C⫶C)=0. f(CH) =15. f(C·O)=18·5 and 15.

f(C:O)=53. f(C·N)=0. f(C:N) =0. f(C⫶N)=0. f(OH) =29·5.

f(O·O)=−10. f(O·N)=0. f(O:N) =0. f(NH) =3·8. f(SH)=2·5.

f(C·S) =0. f(C:S)=9. f(N·N) =0.

The association of the bindings C·O and C:O in one atom of C causes an evolution of 15 ; and the association of two bindings C:O in one atom of C causes an evolution of 30 ; the conversion of tetrad to dyad C causes an evolution of 15. The introduction of a second N:O binding into an N atom connected with C or with O connected with C causes an evolution of 10.

The first point to be noticed in these results is that the functions f(RS) cannot be taken to have the form Ψ(R)Ψ(S), as we found to be the case when R is a metal and S a halogen: in fact the data are too few to give any reliable cue to the form of the functions. But as regards their numerical values, the second point to be noticed is that zero occurs eight times, zero standing for a value too small to be assigned in the present state of thermochemical analysis. The third point is that the value 15, or nearly 15, occurs six times ; while the value 29·5 is nearly twice 15, and 53 nearly three and a half times 15. Of the remaining values one is 3·8, which is almost exactly a quarter of 15 ; another is 18·5, which exceeds 15 by almost a quarter of 15; and the rest are −10, 10, 2·5, and 9. Thus it appears that nearly all the values could be expressed as multiples of a quarter of 15, that is of 3·75, or nearly 3·8. Now at the end of Part I., in discussing the values of (R) for the metals, it was found that on dividing them by 3·8 the results suggested that (R) for the metals is a multiple of 3·8, with some indication of law amongst the multiples. By an accidental coincidence it happened that in studying f(RS), when S is a halogen and R any metal, we found f(RCl) − f(RBr) + f(RCl) − f(RI) or 2f(RCl) − f(RBr) − f(RI) to be a series of multiples of 3·8, with indications of law among the multiples. There is, therefore, rather strong evidence for the hypothesis that atoms, in combining chemically with one another, give forth integral numbers of a certain unit of heat, which may be called the atomic thermochemical unit.

As such an hypothesis, if true, would be of fundamental importance to chemical and physical philosophy, it is to be desired that it should be thoroughly tested by experiment. Indeed it appears that the present need on the experimental side of thermochemistry is the determination of the heat of formation of all the typical organic compounds, and of the first few members of the homologous series derived from them, with some reliable estimate of the probable error of each value. The first grand general survey of the experimental region of thermochemistry has been carried out by such experimenters as Favre and Silbermann, Andrews, Berthelot, Thomsen, Stohmann, Louguinine, and others, to whom we owe the fine existing body of thermochemical data; but it is now time that those who wish to carry on their work should take up the details and establish for the thermochemical constants of bodies as reliable determinations as the skilled analyst can give of their percentage composition.

The existing data for the heat of combustion of a large number of organic compounds as liquids and solids, such as have been determined by Stohmann and his pupils, and Louguinine and others, could be made available for the theoretical study of their heats of formation as gases, by the calculation of their latent heats of vaporization, according to the equation given in the introduction to the present paper, and the use of approximate values of their specific heats as vapours, if it is desired to reduce all results to a temperature of 18° C. But the discussion of such results will probably be more profitable after the fundamentals of the subject have been more thoroughly investigated.

Melbourne, July 1894.

II. *A Theory of the Synchronous Motor.*
By W. G. RHODES, *M.Sc.**

1. SEVERAL foreign writers, notably Steinmetz †, have given theories of the synchronous motor, but most of them, by failing to see how the analysis could be simplified, add to the difficulties of the theory by mathematical intricacies which are apparently quite unnecessary. The author offers the following attempt to present a theory of the synchronous motor in as simple a way as possible, and as the mathematics for the most part consists of simple algebra, the difficulties are reduced to a physical conception of the subject. Many of the results have already been obtained, and the part for which the author

chiefly claims originality is the method of attacking the problem.

2. We consider the case of an alternating-current machine whose field is excited by a direct current, while a simple alternating current passes round the armature.

Let p = output of motor ;

$\quad c$ = virtual value of armature current ;

$\quad R$ = resistance of armature ;

$\quad E$ = virtual value of impressed E.M.F. ;

$\quad e =\quad$,,$\quad$,,$\quad$ counter E.M.F. ;

$\quad L$ = coefficient of self-induction of armature ;

$\quad n$ = frequency of armature current ;

$\quad I$ = impedance of armature = $\{R^2 + (2\pi nL)^2\}^{\frac{1}{2}}$;

$\quad S$ = reactance = $2\pi nL$;

$\quad \psi$ = phase-difference between c and E ;

$\quad \phi =\qquad$,,$\qquad\qquad$,,$\qquad$ c and e ;

$\quad \theta =\qquad$,,$\qquad\qquad$,,$\qquad$ c and Ic.

$\qquad$ Then $\qquad$ the input = $p + c^2 R$;

$$\text{and also} = cE \cos \psi ;$$

therefore $\qquad\qquad p + c^2 R = cE \cos \psi.$

Solving for c we get

$$c = \frac{E}{2R} \cos \psi \pm \frac{1}{2R} \sqrt{\{E^2 \cos^2 \psi - 4pR\}}. \quad . \quad . \quad . \quad (1)$$

Since c is always real, we must have

$$E^2 \cos^2 \psi \geqq 4pR ;$$

therefore the maximum value of p is

$$p = \frac{E^2}{4R}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

This occurs when $\psi = 0$; that is, when the current and the impressed E.M.F. are in phase with each other.

3. We notice that the maximum output is the same as the maximum energy which can be given to an external circuit by a generator of constant E.M.F., E. From (1) we get the corresponding value of the current

$$c = \frac{E}{2R}. \quad . \quad . \quad . \quad . \quad . \quad (3)$$

To find the corresponding value of e we notice that E, e, and Ic (the resultant of Sc and Rc reversed) are in equilibrium

Fig. 1.
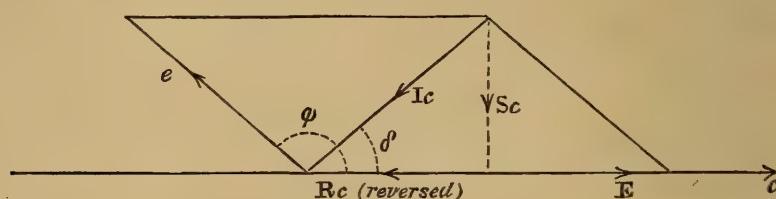
amongst themselves ; so that taking components of these along and at right angles to the direction of E, we have

$$-e \cos \phi = \text{E} - \text{R}c \Big\} ;$$

and
$$e \sin \phi = \text{S}c$$

therefore
$$e \cos \phi = 2\text{R}c - \text{R}c = \text{R}c \Big\}$$

and
$$e \sin \phi = \text{S}c$$

from (3).

Squaring and adding, we get

$$e^2 = (\text{R}^2 + \text{S}^2)c^2 = \text{I}^2 c^2,$$

therefore

$$e = \text{I}c = \frac{\text{IE}}{2\text{R}}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

Also, by division,

$$-\tan \phi = \frac{\text{S}}{\text{R}} = \tan \theta \text{ (see fig. 1).}$$

4. We thus find that when working at maximum output :—

(1) The impressed E.M.F. is in phase with the current in the armature.

(2) The maximum output is $p = \dfrac{\text{E}^2}{4\text{R}}$.

(3) The corresponding current in armature is $c = \dfrac{\text{E}}{2\text{R}}$.

(4) The corresponding counter E.M.F. is $e = \dfrac{\text{IE}}{2\text{R}}$.

(5) The angle of phase between the armature-current and the E.M.F. necessary to overcome the resistance and self-induction of the armature is equal and opposite to the angle between the current and the counter E.M.F.

(6) Also from (4) we see that

$$e \gtreqless E \text{ according as } I \gtreqless 2R,$$

that is according as $(2\pi n L)^2 + R^2 \gtreqless 4R^2,$

$$\text{''} \qquad \text{''} \qquad L^2 \gtreqless \frac{3R^2}{4\pi^2 n^2},$$

$$\text{''} \qquad \text{''} \qquad L \gtreqless \frac{R\sqrt{3}}{2\pi n}.$$

Running Light.

5. We have

$$p + c^2 R = cE \cos \psi \quad \}$$
and
$$p = ce \cos \phi \quad \} .$$

If we neglect the friction of the bearings &c., we may, in this case, put $p = 0$; we then have

$$\phi = \pm \frac{\pi}{2}$$
and
$$cR = E \cos \psi.$$

Hence the maximum value of c is (putting $\psi = 0$)

$$c = \frac{E}{R},$$

the same as would be produced by a constant E.M.F. E in a non-inductive circuit of resistance R.

Also putting $\psi = \pm \frac{\pi}{2}$, the minimum current is zero.

Now, from fig. 1, we get (of course E and c are not now in phase)

$$E^2 = e^2 + I^2 c^2 + 2Ice \cos(\theta - \phi);$$

when $\phi = \pm \frac{\pi}{2}$, this becomes

$$E^2 = e^2 + I^2 c^2 \pm 2Ice \sin \theta$$
$$= e^2 + I^2 c^2 \pm 2Sce, \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

since $\sin \theta = \dfrac{S}{I}$.

The upper sign in (5) corresponds to the machine running as a generator, and the lower sign as a motor.

We also see from (5) that corresponding to $c = \dfrac{E}{R}$ we have

$$e = \mp \frac{ES}{R},$$

and, corresponding to $c = 0$, we have

$$e = \pm E.$$

Now, solving equation (5) as a quadratic in c we get

$$c = \mp \frac{eS}{I^2} \pm \frac{1}{I^2} \sqrt{(I^2 E^2 - R^2 e^2)}, \quad \cdot \quad \cdot \quad \cdot \quad (6)$$

and, as c is real, we must have

$$I^2 E^2 \geqq R^2 e^2$$

or $\qquad\qquad\qquad\qquad IE \geqq Re \, ;$

therefore the maximum value of e is given by

$$e = \pm \frac{IE}{R}$$

and the corresponding current is

$$c = \mp \frac{eS}{I^2}$$

$$= \mp \frac{SE}{RI}.$$

The equation

$$e^2 - 2Sce + I^2 c^2 = E^2$$

is the characteristic curve of the motor running light. It may be written

$$e^2 - 2Sce + S^2 c^2 + R^2 c^2 = E^2$$

or $\qquad\qquad (e - Sc)^2 + R^2 c^2 = E^2,$

or $\qquad\qquad \dfrac{(e - Sc)^2}{E^2} + \dfrac{c^2}{\dfrac{E^2}{R^2}} = 1,$

which is the equation to an ellipse having as conjugate diameters the lines

$$e - Sc = 0 \quad \text{and} \quad c = 0.$$

Similarly, the equation

$$e^2 + 2Sce + I^2 c^2 = E^2,$$

which refers to the generator, may be written

$$\dfrac{(e + Sc)^2}{E^2} + \dfrac{c^2}{\dfrac{E^2}{R^2}} = 1,$$

also the equation to an ellipse. These ellipses are represented in fig. 2.

Fig. 2.
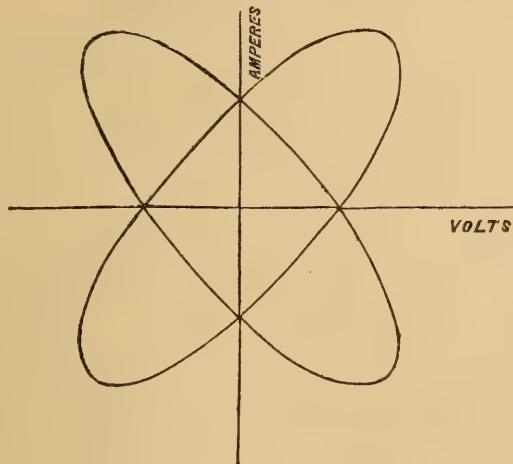
Minimum Current at Given Power.

6. We have
$$p + c^2 R = E c \cos \psi.$$

The current is a minimum when $\dfrac{dc}{d\psi} = 0$. Now, differentiating with respect to ψ,

$$(2cR - E \cos \psi) \frac{dc}{d\psi} + E c \sin \psi = 0 ;$$

therefore, when $\dfrac{dc}{d\psi} = 0$, we have

$$\sin \psi = 0,$$

or
$$\psi = 0 ;$$

that is, the current is a minimum when in phase with the impressed E.M.F., as is otherwise obvious. Putting, therefore, $\psi = 0$, we have

$$p + c^2 R = E c. \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

This curve is of the second degree in c and p, and is satisfied by the following system of points :—

$$(a) \; \left.\begin{array}{l} c = 0, \\ p = 0, \end{array}\right\} \qquad (b) \; \left.\begin{array}{l} c = \dfrac{E}{2R}, \\ p = \dfrac{E^2}{4R}, \end{array}\right\} \qquad (c) \; \left.\begin{array}{l} c = \dfrac{E}{R}, \\ p = 0. \end{array}\right\}$$

That the equation is satisfied by (*a*) is obvious, and we see that it is satisfied by the points (*b*) and (*c*) by writing it in the form

$$\left(c - \frac{E}{2R}\right)^2 + \frac{p}{R} = \frac{E^2}{4R^2}.$$

7. Thus we see that the curve of minimum current at given power passes through the points of

(*a*)   zero current and zero power ;
(*b*)   maximum power ;
(*c*)   maximum current and zero power.

We notice that the maximum current at no load is $c = \dfrac{E}{R}$, whereas if the motor were at rest the current would be $c = \dfrac{E}{I}$; that is, the maximum current at no load is in all cases greater than the maximum current if the armature is at rest.

8. Again, from the equation

$$p + c^2 r = cE \cos \psi$$

we have

$$\psi = \cos^{-1} \frac{p + c^2 r}{cE},$$

therefore

$$\frac{d\psi}{dc} = \frac{c^2 r - p}{c \sqrt{\{c^2 E^2 - (p + c^2 r)^2\}}}$$

$$= 0$$

when

$$p = c^2 r.$$

ψ is then a maximum, and we see that the maximum difference of phase between the current and the impressed E.M.F. takes place when the electrical efficiency is $\frac{1}{2}$.

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9. *Example.*—Suppose we have a 50 kilowatt motor driven by a 1000 volt generator, and suppose that R = 3 ohms and S = 4 ohms, so that I = 5 ohms.

Then maximum output . . $= \dfrac{10^6}{12} =$ 83·3 kilowatts.

Corresponding current . . $= \dfrac{1000}{6} =$ 166·7 amperes.

„   counter E.M.F. $= \dfrac{5000}{6} =$ 833·3 volts.

Maximum current running light $= \dfrac{1000}{3} =$ 333·3 amperes.

Corresponding counter E.M.F. $= \dfrac{4000}{3} = 1333·3$ volts.

&c.

10. To find the characteristic of the motor at any given load we must eliminate θ and ϕ between the equations

$$p = ce \cos \phi,$$

$$\left. \sin \theta = \frac{S}{I}, \right\}$$

and $$E^2 = e^2 + I^2c^2 + 2Ice \cos(\theta - \phi).$$

The eliminant is

$$E^2 - e^2 - I^2c^2 - 2Rp = 2S \sqrt{c^2e^2 - p^2}, \quad . \quad . \quad . \quad (8)$$

which is the required general relation between e and c.

11. In the paper referred to above, Steinmetz calls equation (8) the Fundamental Equation of the Synchronous Motor: the equation is there developed and plotted; results are obtained directly from equation (8), but the development is so cumbrous that the writer thinks that his simple treatment may benefit those interested in the subject of Alternate Current Motors.

III. *Contribution to the Theory of the Robinson Cup-Anemometer. By* C. CHREE, *M.A.*[*]

§ 1. THE velocity of the wind during a hurricane is one of those items of information that, like the speed of express trains, is a source of general interest. The question of the accuracy to be expected in such definite statements as that the wind has blown at 60 miles an hour, though of much less general interest, is still of some practical importance. The usual instrument for the measurement of wind-velocities in this country is the Robinson[†] cup-anemometer. This consists fundamentally of four hemispherical cups attached to arms, inclined to each other at angles of 90° in a horizontal plane, the cups moving under the influence of the wind round a vertical axis. The number of revolutions of the cups in a given time is the information which the instrument, if properly constructed, could be relied on to give. The information desired, however, is what is the time-integral of the wind's velocity. To obtain this it is usually assumed that the wind's velocity is deducible by multiplying that of the centres of the cups by a constant "factor," and the recording mechanism is arranged so as to give the result of this multiplication. The value originally proposed for this factor by Dr. Robinson was 3, and this is the value generally employed in reducing results

[*] Communicated by the Author.
[†] So called after Dr. Robinson of Armagh.

from the " Kew " or standard pattern.   It is pretty generally suspected * that a lower value for the constant would give more accurate results.   Formulæ involving two or three constants have also been proposed and applied in experimental investigations by Robinson, Dohrandt (*l. c.*), Stelling †, Dubinsky ‡, and others, but they have not come into general use, at least in this country.

Experiments involving comparisons of different anemometers have been fairly numerous.   An account of the principal ones prior to 1887 is given by Professor Cleveland Abbe in the ' Report of the Chief Signal Officer of the Army to the Secretary of War,' part ii., Washington 1887, and a bibliography of the subject has been given more recently by Mr. Dines on pp. 36–37 of vol. xvi. of the ' Quarterly Journal of the Royal Meteorological Society.'   More recent investigations have been carried out by Mr. Dines himself in papers printed in the ' Proceedings ' of the Royal Society and the ' Quarterly Journal § of the Royal Meteorological Society.'

A study of some of the literature of the subject has led me to think that a critical examination into certain theoretical aspects of the Robinson cup-anemometer may be of service.

Nature of the Problem.

§ 2. For a final treatment we require in the first instance an exact determination of the physical conditions.   This involves a knowledge of the true values of the normal and tangential forces experienced by the Robinson cups and arms during slow or rapid motion through the air, and also of the frictional forces which arise during the relative motion of the variously lubricated metal surfaces.

The cups, be it remembered, are not travelling in straight lines inclined at a constant angle to the wind's direction, but rotate round an axis whose distance from the centres of the cups is not a very large multiple of their diameters.   Thus at any given instant the relative velocity of the wind to a cup's surface varies appreciably over the cup, and even when the wind is steady the relative velocity at any one point on the surface is continually changing.

The superficial area of the arms and the accompanying stays is usually small relative to that of the cups, but in a

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* See for instance p. 27 of a paper by Dohrandt in *Repertorium für Meteorologie*, Bd. vi. Heft i. ; also " Report of Wind Force Committee," drawn up by Mr. Dines, ' Quarterly Journal Roy. Met. Soc.' vol. xvi. pp. 26 *et seq.*

† *Rep. für Meteorologie*, Bd. ix.   ‡ *Ibid.* Bd. xi.

§ See specially vol. xviii. p. 165.

complete theory the wind's action on the arms and stays should be taken into account.

The frictional forces are exerted on the supports, the rotating vertical axis, and any machinery driven by the arms. These forces are of at least two distinct kinds. Supposing no wind to blow, but the cups rotated by hand, there is a frictional force such as exists when a heavy body rotates on a horizontal table. When wind blows, the rotating vertical axis is pressed against the surfaces guiding it, with a force which is practically equal to the resultant of the horizontal forces exerted at the time by the wind on the cups, stays, and arms. The first mentioned frictional force depends on the weight of the instrument, the latter on the force of the wind, and both on the state of the lubricant.

When, as in some experimental comparisons, the anemometer is mounted on a whirling machine, with its axis at a considerable distance from the axis of rotation of the whirler, the " centrifugal force " calls into play a third frictional force. These facts were clearly pointed out by Dr. Robinson * in describing his experiments.

§ 3. The action of the wind on the cups and arms is presumably of two kinds—tangential viscous action and normal pressure. If the air were a " perfect fluid," only the latter would exist ; but doubtless in practice there is always a certain amount of viscous action. For slow motion it is usual to assume such action proportional to the first power of the relative velocity. But it must, I think, be regarded as somewhat doubtful whether this law is a sufficiently correct representation of the facts for velocities such as 100 feet per second, a value which is sometimes exceeded by the velocity of a Robinson cup relative to the wind in a gale.

As regards the normal pressure, the assumption used to be made that it varied at each point of a solid's surface as the square of the normal component of the relative motion of the undisturbed fluid, irrespective of the shape or size of the solid, or the relative velocity elsewhere than at the point considered. It is now supposed, however, that when the solid surface has a sharp edge discontinuity is set up in the fluid, the nature of the discontinuity and the resultant of the normal pressures depending on the shape of this edge.

Until some mathematically complete solution has been obtained for some practical three-dimensional case, and numerical allowance can be made for the departure of existing fluids from the " perfect " state, comparison of theory and

* Phil. Trans. for 1878, pp. 788–793.

experiment can hardly be absolutely conclusive. The comparison instituted by Mr. Dines * between the experimental results he has found for a long narrow blade moving in air and the formula established by Lord Rayleigh for an infinitely long rectangular lamina, which a stream of perfect liquid meets normally or obliquely, shows apparently a pretty fair *qualitative* † agreement. But experiments under considerably more varied circumstances would be required to determine how closely the one set of results accorded with the other.

The application of Lord Rayleigh's formula to ordinary square and rectangular plates, instances of which are recorded by Prof. Cleveland Abbe (*l. c.* p. 243), is, it need hardly be said, entirely without mathematical warrant.

The desirability of the solution of some simple three-dimensional problem is increased by some recent contributions of Lord Kelvin's to ' Nature ' ‡, if they are intended, as seems the case, to throw doubt on the views of discontinuity in fluid-motion current since Kirchhoff's treatment of the subject.

While the exact formula for the resultant force experienced by a finite solid moving in a perfect liquid is not known, there is at least a pretty strong *à priori* probability § that it depends on the square of the relative velocity, so long at least as the velocity is small compared to that of sound in the medium, and the body's course does not cross its own wake. With the Robinson cups in air the former condition is satisfied, the latter perhaps hardly, especially in short-armed instruments. In experiments on whirlers, where the air is naturally at rest and the cups in motion, a very perceptible current has been observed by Robinson ‖, Dohrandt ¶, and others. In ordinary use the wind's velocity so much exceeds that of the cups, that if there were only a single cup an appreciable effect of this kind could hardly arise. In the actual case of four cups it can hardly be doubted, however, that during part at least of its course the wind's action on any one cup is modified by the presence of the others, and when the arms are short the neglect of this interference might possibly lead to serious error.

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* Proc. Roy. Soc. vol. xlviii. pp. 254–257.
† See, however, Lord Kelvin, ' Nature,' vol. l. pp. 574–5.
‡ Vol. l. 1894, pp. 524, 549, 573, 597.
§ *Cf.* Professor Stokes in Appendix to Dr. Robinson's paper, Phil. Trans. for 1878, p. 819.
‖ *Cf.* Dr. Robinson, Phil. Trans. 1878, pp. 783 *et seq.*
¶ *Repertorium für Meteorologie,* Bd. iv. Heft i. (see p. 32 of paper) & Bd. vi. Heft 1.

Wind's Driving-Action.

§ 4. To get a preliminary *general* idea of the driving action of the wind, let us suppose each Robinson cup replaced by a thin plank, infinitely long in the vertical direction and of horizontal breadth b, the planes of the planks intersecting— if we imagine them continued inwards—in the axis of rotation, and suppose each plank attached to a horizontal arm of negligible section. Let each arm and plank be rotated with negligible velocity round the vertical axis, while a horizontal wind blows with uniform velocity v. Let α denote the inclination of the wind to the normal to the plank ; then, treating the air as a perfect liquid, we have, by Lord Rayleigh's formula[*], for the driving-force per unit length of plank,

$$F = \frac{\pi\rho V^2 b \cos\alpha}{4 + \pi \cos\alpha}, \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (1)$$

where ρ is the air's density. F acts normally to the plank at a distance

$$z = 3b \sin\alpha / \{4(4 + \pi \cos\alpha)\} \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (2)$$

from the central vertical line of the plank, on the side on which the direction of the wind makes an acute angle with the surface. There is thus a couple about the axis of rotation whose value per unit length of plank is

$$G = \frac{\pi\rho V^2 b \cos\alpha}{4 + \pi \cos\alpha}(l + z), \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (3)$$

where l is the distance of the central line of the plank from the axis of rotation. The angle α, and thus z, is to be taken as positive when the direction of the incident wind makes an acute angle with the horizontal line drawn from the plank's centre outwards along the surface from the axis of rotation. There is a continual variation in the magnitude of the resultant force and couple, and the centre of pressure moves from one side to the other of the central line every half revolution. The distance between the extreme positions of the centre of pressure is no less than $3b/8$. The wind-pressure, it will be noticed, aids the motion in one half-revolution and opposes it in the other.

Suppose, next, the plank and arm to rotate round uniformly, the velocity v at the central line of the plank being comparable with though less than V. The direction of v is perpendicular of course to the arm. Let us first find the

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[*] See Basset's ' Treatise on Hydrodynamics,' vol. i. art. 138.

magnitude and direction of the relative velocity of the wind
to the plank at its central line.
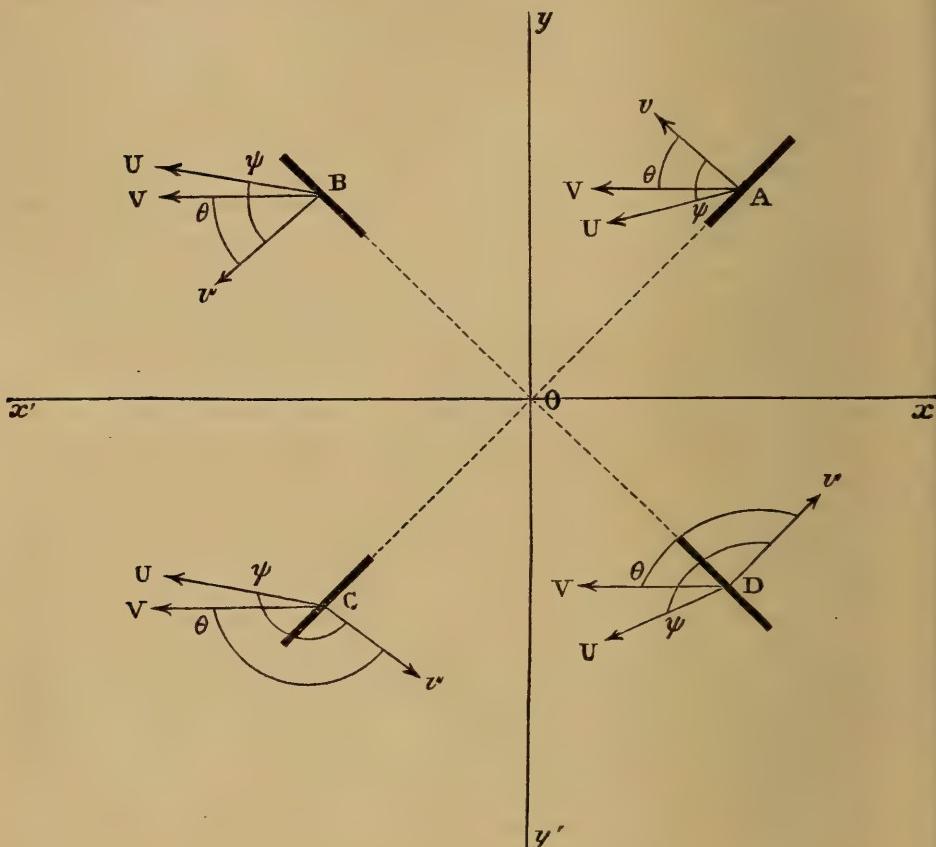
The figure represents the horizontal plane in which moves
a given point in the plank's central line.   O is the centre of
rotation ; $x\,O\,x'$ the direction the wind blows in.   The rotation
is from x to y.   A, B, C, D represent four positions of the plank.
U is the velocity of the wind relative to the plank at its central
line. θ and ψ denote the inclinations of the directions of V
and U to the normal to the plank drawn always in the direction
in which the plank moves.   The relations

$$\left.\begin{array}{l} U^2 = V^2 + v^2 - 2Vv\cos\theta, \\[2mm] \cot\psi = \cot\theta - \dfrac{v}{V}\,\mathrm{cosec}\,\theta, \end{array}\right\} \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (4)$$

hold obviously throughout the motion.
    If the breadth b be very small compared to the distance l
of the plank's central line from the axis of rotation, the
velocities v and U may practically be supposed to apply over
the whole plank.   But even then there is one obvious objection

to the application of Lord Rayleigh's formula, in addition to those previously considered, viz. that the stream-lines cannot at once assume the positions given them by an equilibrium-theory.

Taking the equilibrium-values in default of better, we obtain the resultant force and couple per unit length of plank by writing U^2 for V^2 and ψ for α in (1) and (3). The wind's action, it should be noticed, no longer aids the motion throughout a whole half revolution, but only through an angular interval $\cos^{-1}(v/V)$ on *each* side of Oy. As v/V increases this angle continually diminishes, vanishing of course in the limit when $v = V$.

When b/l is not small the problem, even from the equilibrium standpoint, becomes much more complicated. In the positions A and B in the figure, the velocity of the wind relative to the plank decreases as the distance from O increases, the reverse holding in the positions C and D. The natural thing might seem to be to assume Lord Rayleigh's result as holding for successive narrow parallel strips of the plank, and then integrate * the elementary couples so found across the width b. It is quite possible the result thus obtained might be fairly accurate, but it is perhaps quite as likely it might not. Until the problem actually presented has been satisfactorily solved, certainty cannot be reached by any amount of general reasoning.

So long as b/l though not negligible is decidedly small, I suspect the best one can do in our present state of knowledge is to take for the resultant pressure and couple the values found by regarding U as everywhere the same as at the central line.

It may perhaps be as well to point out that as the relative velocity, for a uniform v, is greatest when the motion is against the wind, the wind's action necessarily tends to diminish an initial velocity in a symmetrical body like a plank with equal plane faces.

§ 5. All the difficulties we have noticed in connexion with the imaginary infinite planks present themselves in the case of the Robinson cups, and most of them in an accentuated form. The pressure experienced by a hemispherical cup moving through a perfect liquid has not been determined mathematically, even for the simplest case when the wind's direction is along the axis of the cup, *i. e.* is perpendicular to the plane base of the hemisphere. The absolute velocity, answering to the

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* A process similar to this is adopted by Prof. G. H. L. Hagen in a paper in the *Abhandlungen* of the Berlin Academy, the original of which I have not seen. This paper is reprinted in Prof. Cleveland Abbe's ' Mechanics of the Earth's Atmosphere ' (see p. 20).

rotation, varies from point to point of the surface, not merely in intensity but also, especially in short-armed cups, in direction. Unlike a plane plank, whose two faces are symmetrical, the cup experiences very different resultant pressures according as its concavity or its convexity faces the wind. According to Dines * the resultant pressures in the two cases, apparently for wind along the axis, are in the ratio 132 : 45 for a 9-inch cup and 126 : 55 for a 5-inch cup. Without a difference of this kind the cups of course would not go round.

Theoretical Investigation by Thiesen.

§ 6. Of the theoretical investigations into the behaviour of the Robinson cup-anemometer, discussed by Prof. Cleveland Abbe, much the most complete appears to be that of Thiesen (*l. c.* pp. 294–300). This is of importance for our present object, so I give a brief outline of the method of treatment, deduced from a personal study of the original paper †. Instead of Thiesen's notation, l, ρ, V, v, U, θ, ψ are employed as in § 4. The angle θ, when the cup is in motion, measures, it will be noticed, the angular position of the arm of a cup, as well as the inclination of the wind's direction to the axis. Thiesen assumes that what he calls the "normal" component of the wind's velocity is alone effective ; by this he means the component along the axis of the cup. His argument proceeds as follows :—

(*a*) Suppose that when the wind's direction makes an angle θ with the axis of a cup at rest, the resultant normal pressure is $\rho \mathrm{V}^2 \mathrm{R}^2 f(\theta)$, where R is the radius of the cup, $f(\theta)$ an unknown function of θ.

(*b*) Then when the cup is in motion the resultant normal pressure is $\rho \mathrm{U}^2 \mathrm{R}^2 f(\psi)$, and the resultant driving couple $\rho \mathrm{U}^2 \mathrm{R}^2 l f(\psi)$.

(*c*) The angular velocity of the arm is

$$\frac{d\theta}{dt} = \frac{v}{l} = \frac{\mathrm{V}}{l}\left(\frac{v}{\mathrm{V}}\right);$$

also

$$\frac{d^2\theta}{dt^2} = \frac{1}{2}\frac{d}{d\theta}\left(\frac{d\theta}{dt}\right)^2$$

$$= \tfrac{1}{2}\left(\frac{\mathrm{V}}{l}\right)^2\frac{d}{d\theta}\left(\frac{v}{\mathrm{V}}\right)^2,$$

supposing the wind's velocity to have a constant value. Thus,

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* Royal Society's ' Proceedings,' vol. l. 1891, p. 51.
† *Repertorium für Meteorologie*, Bd. v. Heft 2 (1877).

I being the moment of inertia round the axis of rotation, the equation of motion is

$$\mathrm{I}\left(\frac{\mathrm{V}}{l}\right)^2\left(\frac{v}{\mathrm{V}}\right)d\left(\frac{v}{\mathrm{V}}\right)=\rho\mathrm{U}^2\mathrm{R}^2lf\left(\psi\right)d\theta. \quad . \quad . \quad (5)$$

Supposing 4 cups and arms, there would really exist 4 terms on the right, each deducible from the previous by writing $\frac{\pi}{2}+\theta$ for θ.

Eventually a *steady* state will be reached in which $\left(\frac{v}{\mathrm{V}}\right)$ will be a pure periodic function of θ, and so the left-hand side of (5) must vanish when integrated from $\theta=0$ to $\theta=2\pi$. Consequently, we must have also

$$\int_0^{2\pi}\mathrm{U}^2f(\psi)d\theta=0. \quad . \quad . \quad . \quad . \quad . \quad (6)$$

(d) It is clear that in an anemometer in which I is considerable v/V is very nearly constant during a revolution; thus to a first approximation constancy may be assumed. On this assumption (4) gives

$$d\theta=\frac{\mathrm{U}}{\mathrm{V}}\left(1-\frac{v^2}{\mathrm{V}^2}\sin^2\psi\right)^{-\frac{1}{2}}d\psi; \quad . \quad . \quad . \quad (7)$$

and so, as V is supposed constant, we can replace (6) by

$$\int_0^{2\pi}\left(\frac{\mathrm{U}}{\mathrm{V}}\right)^3\left(1-\frac{v^2}{\mathrm{V}^2}\sin^2\psi\right)^{-\frac{1}{2}}f(\psi)d\psi=0, \quad . \quad . \quad (8)$$

where U/V may be regarded as a function of ψ from the geometrical relation

$$\frac{\mathrm{U}}{\mathrm{V}}=\left\{1-\left(\frac{v}{\mathrm{V}}\right)^2\sin^2\psi\right\}^{\frac{1}{2}}-\frac{v}{\mathrm{V}}\cos\psi. \quad . \quad . \quad (9)$$

(e) It is assumed that

$$f(\psi)=f(-\psi)=\mathrm{A}_0+\mathrm{A}_1\cos\psi+\mathrm{A}_2\cos 2\psi+\ldots, \quad . \quad (10)$$

where A_0, A_1, &c., are constants.

(f) Suppose that if v/V be treated in (8) as constant, the proper value to assign it is $2a$. Then substituting $2a$ for v/V, and employing the series for $f(\psi)$, expand the quantities under the integral sign in (8) in powers of a and integrate. There results to determine a the equation

$$\mathrm{A}_0-3a\mathrm{A}_1+4a^2(\mathrm{A}_0+\mathrm{A}_2)-\tfrac{1}{2}a^3(3\mathrm{A}_1+5\mathrm{A}_3)+\ldots=0. \quad . \quad (11)$$

As a is supposed to be as small as 1/6, presumably a few

terms will suffice to give its approximate value, assuming, of course, the A's to be known.

Thiesen then proceeds to correct the approximation $2a$ to the value of v/V as follows :—

(α) There is a correction to allow for the fact that v/V is really a periodic function of θ, the periodic part vanishing when I is infinite.

(β) There is a correction to allow for the velocity due to the rotation being really variable over the cup, and for the centre of pressure being variable in position.

(γ) There is a correction to allow for the wind's action on the arms.

(δ) It is stated that the hypotheses in (a), that the resultant pressure varies as the area of the cup and as the square of the wind's velocity, are neither strictly true. It is apparently concluded, however, that the deviation from these laws would not affect the value found for v/V to the degree of approximation attained.

(ϵ) There is a correction for the frictional forces of the two classes specified above, one force proportional to the weight of the apparatus, the other to the resultant horizontal force exerted by the wind on the movable parts.

There are, it must be confessed, a good many doubtful points in the investigation. The whole system of applying corrections is open to criticism, unless definite evidence can be produced that the differences between the original theory and the physical facts are small. In the present case one is not in a position to affirm that all the divergences for which corrections are applied are small in any given type of instrument, and it may be doubted whether the forms the corrections are supposed to take are necessarily correct.

The degree of convergency of the series in (11) is very uncertain. The correction (ϵ) is supposed to introduce a couple opposing the motion, of the form

$$v(\beta + \gamma \mathrm{V}^2),$$

where β and γ are constants, and this is manipulated so as to appear as equivalent to a variation in the value of the constant A_1 appearing in (11). I do not see how the coefficient v is accounted for by the ordinary laws of friction, and should have expected the coefficient of γ to be U^2 instead of V^2. The method of treating the friction as a correction would be of course wholly unjustifiable unless it were a comparatively unimportant item.

As none of the constants A are really known, and the various corrections introduce fresh quantities likewise un-

known, the outcome of the mathematical work—which is of considerable merit—is of somewhat doubtful practical utility. At the same time the paper seems to show the line a complete mathematical solution might take if fuller experimental knowledge existed.

Deduction of an Equation of Motion.

§ 7. I now propose to look at the matter a little differently. The couples acting on the instrument at any instant are primarily three :—A couple such as $\rho U^2 R^2 l f(\psi)$ in (b), where $f(\psi)$ may be in reality a function of R, R/l, and v/V. A couple $-(\beta + \gamma U^2)$ arising from the friction opposing the motion, where γ is probably a function of R, R/l, and v/V, but not of the mass turning ; β is proportional to the mass turning. A couple arising from the viscous action of the wind which may be taken as opposing the motion. Provisionally it may be supposed to be of the form

$$- KV - K'v,$$

where K and K′ are constants.

During a revolution of the cups v is usually nearly constant—more nearly so than V, most probably, as a rule. Thus we may expect to approximate closely to the true motion by treating the driving force as having at any instant the mean value it would possess throughout a complete revolution during which V and v retained unchanged their instantaneous values*. The equation of motion so derived would be

$$\frac{dv}{dt} = l\frac{d^2\theta}{dt^2} = \frac{1}{2\pi I}\int_0^{2\pi}\left[\rho U^2 R^2 l^2 f(\psi) - l(\beta + \gamma U^2) - l(KV + K'v)\right]d\theta. \quad (12)$$

If $f(\psi)$ and γ be assumed to contain only integral powers of v/V we should, assuming expansion possible, obtain an equation of the type

$$\frac{dv}{dt} = -a_0 - a_1 v - b_1 V + V^2\left[c_2 - 2b_2\frac{v}{V} - a_2\left(\frac{v}{V}\right)^2 - c_3\left(\frac{v}{V}\right)^3 \dots\right], \quad (13)$$

where a_0, a_1, &c., are independent of v or V.

Unless we know the forms of $f(\psi)$ and γ we cannot tell whether the series inside the square bracket consists of a finite or an infinite number of terms ; and if it be an infinite series we have no data relative to its convergency.

If the series were infinite it could hardly be convergent in

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* In the ordinary instrument with four equal cups, the entire cycle of changes with respect to the wind's incidence is gone through every quarter revolution, thus the hypothesis involves no greater assumption than that changes in V or v during a *quarter* revolution are small.

the form shown unless v were less than V. Now conditions certainly arise when this is not the case. If, for instance, during a calm the instrument were put in rotation by the hand, and left to itself, there would initially be an infinite value for v/V, and somewhat similar phenomena must occur during a sudden lull after a violent gust of wind.

It is of course possible that one equation of motion holds for values of v/V less than unity, and a totally different equation for greater values. It is difficult, however, to imagine a cause for such discontinuity. The wind, as we have seen, always opposes the cup's motion during the greater part of each revolution. As v/V approaches unity the corresponding physical phenomenon is the contraction of the angular interval throughout which the wind aids the motion. The interval simply vanishes when v/V equals unity and remains zero for all higher values of v/V. There is no suggestion of discontinuity in the physical conditions.

The only simple form of equation suggested by the preceding investigations which is applicable without inconsistency, whether v/V be small or big, is

$$\frac{dv}{dt} = -a_0 - a_1 v - b_1 V - a_2 v^2 - 2b_2 vV + c_2 V^2. \quad . \quad (14)$$

It is assumed of course that neither v nor V can be negative. The term $-a_0$ answers to friction, the full value of which is called into play only when the cups move or are on the verge of motion. The critical wind-velocity V_0 required to call up the full amount of this friction, so as just to prevent motion, is obtained by supposing v and $\frac{dv}{dt}$ in (14) to vanish. The resulting equation is

$$c_2 V_0{}^2 - b_1 V_0 - a_0 = 0. \quad . \quad . \quad . \quad . \quad (15)$$

For values of V less than V_0 only so much friction is called into play as suffices to prevent motion. The possibility of $\frac{dv}{dt}$ being negative, when v is zero, is thus precluded.

§ 8. The reasoning by which we have been led to (14) cannot claim to be conclusive. The formula, though to a certain extent suggested by theory, is admittedly in part empirical, and must be accepted only provisionally. The following are perhaps the strongest points in its favour :—

1. It is, as explained above, strictly in accordance with the observed fact that the cups do not move until the wind has attained a certain velocity.

2. There are no mathematical objections to its use for all possible positive values of v and V.

3. It accords with the fact that if, during a calm, the instrument be set in motion the velocity is gradually reduced to rest.

4. In a uniform high wind it gives to a close degree of approximation a quadratic equation,

$$a_2(v/\mathrm{V})^2 + 2b_2(v/\mathrm{V}) - c_2 = 0,$$

to determine the value of v/V in the steady state, being thus apparently in accordance with Dr. Robinson's experimental conclusions in the 'Philosophical Transactions' for 1878.

It may seem a waste of time to expend further thought on a formula whose basis is so uncertain. This is a view of the case I should certainly adopt if there were reasonable grounds for expecting in the near future an approximately exact mathematical treatment of the problem. The chance of this seems, however, rather remote, and I have thus decided that it is worth while to examine the conclusions to which (14) leads.

The desirability of some attempt to utilize the best existing data will, I think, be recognized by any one who has compared the regular march of the trace given by an ordinary Robinson cup-anemometer with the large and incessant fluctuations in the trace from such an instrument as " Dines' tube-anemometer "*.

§ 9. Before entering on the mathematical treatment of (14) we must justify the signs given the various terms, it being supposed that the coefficients a_0, a_1, ... themselves are all positive.

The motion in a calm is given by

$$\frac{dv}{dt} = -a_0 - a_1 v - a_2 v^2. \quad \ldots \quad (16)$$

If a_2 were a negative quantity, it would be possible, by giving v a sufficiently big initial value, to make $\dfrac{dv}{dt}$ initially positive. The velocity of the cups would then go on continually accelerating, though all the forces acting would be of a frictional or viscous character and would necessarily oppose the motion. The hypothesis that a_2 is negative may thus be rejected. If next we suppose the cups, initially at rest, suddenly allowed to move under the influence of the wind, the motion at the

* Quart. Journ. R. Met. Soc. vol. xviii. pp. 168 *et seq.*

start is given by

$$\frac{dv}{dt} = -a_0 - b_1 V + c_2 V^2. \quad . \quad . \quad . \quad (17)$$

If the wind is high the term $c_2 V^2$ must preponderate, if c_2 be not zero, and v must be positive as the cups always move convexity first : thus c_2 must be positive.

Consider next the equation

$$a_0 + a_1 v + b_1 V + a_2 v^2 + 2 b_2 v V - c_2 V^2 = 0, \quad . \quad . \quad (18)$$

giving the velocity v in the steady state answering to a wind of uniform velocity V. If the wind be high, V/v is very approximately deducible from

$$c_2 (V/v)^2 - 2 b_2 (V/v) - a_2 = 0. \quad . \quad . \quad . \quad (19)$$

Now for any given value of V experiment shows that a steady state is possible. Thus (19) must have a positive root. Now V/v is certainly not less than 2, and so if b_2 were negative it would be necessary for a_2 to be at least 4 times the numerical sum of b_2 and c_2 to allow of (19) having a suitable positive root. Professor Stokes[*], however, in treating of Dr. Robinson's results, decided that they fitted a formula such as (19) best when in it a_2/b_2 and a_2/c_2 were supposed small or even zero. The alternative that b_2 is positive is thus much the most probable. If a_2, b_2, c_2 are, as we suppose, all positive, there is but one change of sign on the left-hand side of (19), a result in accordance with the observed fact that for any given wind-velocity there is only one steady state.

The term $-a_0$ in (14) can hardly answer to anything but a frictional force, presumably between metal surfaces, opposing the motion, so there can be little doubt a_0 is positive.

As to the signs of a_1 and b_1 there is more uncertainty. If a_1 were a negative quantity, then, supposing a_2 small, the right-hand side of (16) might become positive when v lay within certain limits ; this would imply that if, during a calm, the cups were given a suitably selected initial velocity, this velocity would for a time go on accelerating. Such a phenomenon is, to say the least of it, most improbable. The alternative that a_1 is positive seems thus the most probable, and should certainly be adopted if there is reason to believe a_2 zero or very small.

Either sign for b_1 seems to suit all the mathematical criteria equally well, and there is nothing on the physical side to turn the scale. It fortunately does not seem of any importance to

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[*] Phil. Trans. for 1878, pp. 820–1. The formula actually given by Prof. Stokes includes a term answering to a_0 in (18).

our further investigations which is the correct sign, so that there is no necessity to come to a final decision.

The Steady State.

§ 10. The first application to be made of (14) is to the steady state.

In high winds, as already indicated, a close approximation to the value of V/v is supplied by (19). Now for the same anemometer, at least when in a uniform state of lubrication, a_2, b_2, c_2 are constants, so that in high steady winds V/v is practically independent of V.

Each of the coefficients a_2, b_2, c_2 contains a part arising from the wind's driving action which varies with the arm l, and a second part arising from the friction which is associated with the horizontal pressure produced by the wind's action; the latter part is practically independent of l, but varies with the coefficient of friction, and with the arm d at which the frictional forces act. Thus, if two anemometers in which the friction and d/l are widely different give nearly identical values of V/v in high steady winds, then there is a strong presumption that the frictional forces of the species considered are unimportant in both. The ratios $a_2 : b_2 : c_2$ do not depend directly on the weight or inertia of the instrument, so in high steady winds these factors would seem of secondary importance.

In light winds $-a_0-a_1v-b_1V$ may no longer be neglected. The coefficients a_1, b_1 depend presumably rather on the perimeter than the area of the cups, while a_0 depends on the weight and the lubricant. There is thus no apparent reason for expecting in light winds any close agreement between instruments of different patterns variously lubricated. As a matter of fact, in very light winds one anemometer may stand still while another, precisely similar in outward appearance, a few feet distant goes on recording a mile or two an hour.

Some idea of differences in this respect may be derived from the consideration of the wind-velocity V_0 which just suffices to keep the cups turning. This is the positive root of (15), or

$$V_0 = \frac{b_1}{2c_2} + \frac{\sqrt{b_1{}^2 + 4a_0c_2}}{2c_2}. \qquad . \quad . \quad . \quad . \quad (20)$$

Other things being similar, V_0 increases with a_0, and so with the weight of the apparatus and the coefficient of friction. The less limpid the lubricant the larger V_0. Thus in light winds the readings even of one and the same anemometer

cease to be comparable unless the state of the lubricant remains practically constant.

Wind Velocity with small Harmonic Term.

§ 11. Suppose the wind's velocity to vary harmonically with the time according to the law

$$V = \overline{V}(1 + \lambda \cos pt), \quad \ldots \quad \ldots \quad (21)$$

where λ is small. The wind's velocity runs through a complete cycle in the time $2\pi/p$, with maximum and minimum values $\overline{V}(1 \pm \lambda)$ and mean value $\overline{V}$.

Assuming λ^2 negligible, we can satisfy (14) by supposing

$$v = \bar{v}\{1 + \nu \cos(pt - \sigma)\}, \quad \ldots \quad \ldots \quad (22)$$

where

$$a_0 + a_1\bar{v} + b_1\overline{V} + a_2\bar{v}^2 + 2b_2\bar{v}\overline{V} - c_2\overline{V}^2 = 0, \quad \ldots \quad (23)$$

$$\sigma = \tan^{-1} p/\{a_1 + 2a_2\bar{v} + 2b_2\overline{V}\}, \quad \ldots \quad \ldots \quad (24)$$

$$\nu = \lambda \frac{\overline{V}}{\bar{v}} \frac{(2c_2\overline{V} - 2b_2\bar{v} - b_1)}{\sqrt{p^2 + (2b_2\overline{V} + 2a_2\bar{v} + a_1)^2}}. \quad \ldots \quad (25)^*$$

From (22) we see the velocity of the cups has a mean value $\bar{v}$, and has a harmonic variation of the same frequency $p/2\pi$ as the wind but different in phase. From (23) we see that $\bar{v}$ is the velocity the cups would have in the steady state answering to a wind of uniform velocity $\overline{V}$. Thus the deduction of the space traversed by the wind, in a time large compared to $2\pi/p$, from the value of $\int v\, dt$ in the ordinary way is practically as satisfactory in this case as in that of a steady wind.

As to the details of the cups' motion, we see from (24) and (25) that the phase and amplitude of the harmonic term in v depend both on the frequency of the harmonic change in the wind's velocity and the mean value of that velocity.

If the frequency be small and the mean velocity great, then approximately

$$\left. \begin{aligned} \sigma &= 0, \\ \nu &= \lambda \frac{\overline{V}}{\bar{v}} \frac{c_2\overline{V} - b_2\bar{v}}{b_2\overline{V} + a_2\bar{v}}; \end{aligned} \right\} \quad \ldots \quad \ldots \quad (26)$$

thus the harmonic motion of the cups is in the same phase

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* If (14) be written $\dfrac{dv}{dt} + f(v, V) = 0$, then (25) may be written

$$\frac{\nu}{\lambda} = -\frac{\overline{V}}{\bar{v}} \frac{df(\bar{v}, \overline{V})}{d\overline{V}} \div \sqrt{p^2 + \left(\frac{df}{dv}\right)^2}.$$

and of the same order of magnitude as that of the wind. If $\overline{V}/\bar{v}$ be practically constant for different values of $\overline{V}$, then ν/λ is so likewise.

If, on the other hand, the frequency be high and $\overline{V}$ not too big, σ tends towards $\pi/2$, while ν becomes small. This signifies that the time when the cups move fastest tends to approach that when the wind has slowed down to its mean value, but the variation in the cups' velocity is proportionally much less than that in the wind's. In this case the action of the Robinson cups is conspicuously to smooth down the variation actually occurring in the wind's velocity, without introducing appreciable error into the measurement of the total space travelled by the wind.

If the expression for the wind's velocity contained a series of small harmonic terms of different frequencies, conclusions similar to the above would equally apply to each term.

General Solution when a_2 is zero.

§ 12. When a_2 is zero the integral of (14) is known to be[*]

$$v = e^{-\int(a_1 + 2b_2 V)dt}\left\{C + \int(c_2 V^2 - b_1 V - a_0)e^{\int(a_1 + 2b_2 V)dt}\,dt\right\}, \quad . \quad (27)$$

where C is a constant determined by the initial conditions.

When V is a known function of t, v can be evaluated to any required degree of accuracy by quadratures, but the operation will generally be tedious.

As an example, suppose that after the steady state answering to $V = A$ has been attained, V diminishes according to the law

$$V = A - Bt,$$

where B is a constant.

Substituting for V in (27), and determining C so that when $t = 0$ the value of v is that answering to a wind-velocity A in the steady state, *i. e.* is given by

$$v = (c_2 A^2 - b_1 A - a_0)/(a_1 + 2b_2 A), \quad . \quad . \quad . \quad (28)$$

we find

$$v = \frac{c_2 A - b_1}{2b_2} - \frac{c_2 a_1}{4b_2{}^2} - \frac{c_2 Bt}{2b_2} + \left(\frac{c_2 a_1{}^2}{4b_2{}^2} + \frac{a_1 b_1}{2b_2} - a_0\right)\frac{e^{-\left\{(a_1 + 2b_2 A)t - b_2 Bt^2\right\}}}{a_1 + 2b_2 A}$$

$$+ \left\{\frac{c_2 B}{2b_2} + \frac{c_2 a_1{}^2}{4b_2{}^2} + \frac{a_1 b_1}{2b_2} - a_0\right\}e^{b_2 B\left(t - \frac{a_1 + 2b_2 A}{2b_2 B}\right)^2}\int_0^{t} e^{-b_2 B\left(t - \frac{a_1 + 2b_2 A}{2b_2 B}\right)^2}\,dt. \quad . \quad (29)$$

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[*] Forsyth's 'Differential Equations,' p. 18.

The integral appearing here is of the well-known type

$$\int e^{-x^2/h^2}\, dx$$

appearing in the theory of probability.

To determine the mode in which v commences to vary from its initial value (28), expand the several exponentials and retain only lowest powers of t. In this way we find

$$v = \frac{c_2 A^2 - b_1 A - a_0}{2b_2 A + a_1} - \frac{c_2 a_1 A + c_2 b_2 A^2 + b_2 a_0 - \frac{1}{2} a_1 b_1}{2b_2 A + a_1} B t^2. \quad (30)$$

Thus the initial departure of v from its steady value depends on t^2, and so is extremely slow compared to that of V.

If we neglected the terms $a_0 + a_1 v + b_1 V$, we should get in place of (29),

$$v = \frac{c_2}{2b_2}(A - Bt) + \frac{c_2}{2b_2} B e^{b_2 B\left(t - \frac{A}{B}\right)^2} \int_0^t e^{-b_2 B\left(t - \frac{A}{B}\right)^2} dt. \quad (31)$$

This shows that v is always in excess of the value

$$\frac{c_2}{2b_2}(A - Bt)$$

given it on the ordinary or, as we shall term it, *equilibrium* theory.

On the same simplified hypothesis we replace (30) by

$$v = \frac{c_2}{2b_2} A(1 - b_2 B t^2). \quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot \quad (32)$$

In obtaining (29) and (30) we have tacitly assumed that $(B/A)t$ is small as well as t. If the rate of change of V is very rapid, then even when t is very small (32) had better be replaced by

$$v = \frac{c_2}{2b_2} A \left\{ 1 - b_2 B t^2 \left(1 - \frac{2}{3}\frac{B}{A} t\right)\right\}. \quad\cdot\quad\cdot \quad (33)$$

This result may be applied in this case up to the time

$$t = A/B$$

at which V vanishes. For the value of v when V vanishes, it gives

$$v = \frac{c_2}{2b_2} A \left\{ 1 - \frac{1}{3} b_2 A \cdot \frac{A}{B}\right\}. \quad\cdot\quad\cdot \quad (34)$$

a₂ not zero, but V constant.

§ 13. For shortness write (14) in the form

$$\frac{dv}{dt} + a_2(v - v_1)(v + v_2) = 0, \quad\cdot\quad\cdot\quad\cdot\quad\cdot \quad (35)$$

where

$$a_2(v-v_1)(v+v_2) = a_0 + a_1 v + b_1 V + a_2 v^2 + 2b_2 vV - c_2 V^2. \quad (36)$$

It is obvious that v_1 represents the value of v in the steady state answering to the wind-velocity V.

Supposing that initially

$$t = 0, \quad v = v_0,$$

we easily find

$$v = v_1 + (v_0 - v_1) e^{-a_2(v_1+v_2)t} \div \left\{ 1 + \frac{v_0 - v_1}{v_1 + v_2} (1 - e^{-a_2(v_1+v_2)t}) \right\} \quad (37)$$

The space s traversed in time t by the cups' centres is given by

$$s \equiv \int_0^t v \, dt = v_1 t + \frac{1}{a_2} \log \left\{ 1 + \frac{v_0 - v_1}{v_1 + v_2} (1 - e^{-a_2(v_1+v_2)t}) \right\}. \quad (38)$$

From (37) we see that, theoretically, an infinite time is required to assume the final velocity v_1 answering to the steady state.

When t becomes very large, s approaches asymptotically the value

$$v_1 t + \frac{1}{a_2} \log \frac{v_0 + v_2}{v_1 + v_2}.$$

Thus the true run of the cups cannot differ from what is given by the equilibrium theory by more than

$$\frac{1}{a_2} \log \frac{v_0 + v_2}{v_1 + v_2}.$$

§ 14. As an interesting development of the results of the last paragraph, suppose that $v = v_0$ when $t = t_0$, and that thereafter there are alternate intervals T_1 and T_2 during which V has the different constant values V' and V'' respectively.

Let v_1' and v_2' be the values of the v_1 and v_2 of last paragraph which answer to V', and v_1'', v_2'' the values which answer to V''. In the present paragraph we shall employ v_1 to denote the value of v at the end of the first interval T_1, v_2 to denote its value at the end of the succeeding interval T_2, and so on. The corresponding values of s (the space traversed by the cups' centres) are denoted by s_1, s_2, &c.

For brevity we shall write

$$\left. \begin{aligned} e^{-a_2(v_1'+v_2')T_1} &\equiv x', \\ e^{-a_2(v_1''+v_2'')T_2} &\equiv x''. \end{aligned} \right\} \quad . \quad . \quad . \quad . \quad (39)$$

Noticing that the $\overline{2n-1}^{\text{th}}$ and $2n^{\text{th}}$ intervals are of lengths

T_1 and T_2 respectively, and that the values of v at their conclusions are v_{2n-1} and v_{2n}, we see that by (37) and (38)

$$v_{2n-1} = v_1' + x' (v_{2n-2} - v_1') \div \left\{ 1 + (1-x') \frac{v_{2n-2} - v_1'}{v_1' + v_2'} \right\}, \quad (40)$$

$$v_{2n} = v_1'' + x'' (v_{2n-1} - v_1'') \div \left\{ 1 + (1-x'') \frac{v_{2n-1} - v_1''}{v_1'' + v_2''} \right\}, \quad (41)$$

$$s_{2n-1} = v_1' T_1 + \frac{1}{a_2} \log \left\{ 1 + (1-x') \frac{v_{2n-2} - v_1'}{v_1' + v_2'} \right\}, \quad \cdot \quad \cdot \quad (42)$$

$$s_{2n} = v_1'' T_2 + \frac{1}{a_2} \log \left\{ 1 + (1-x'') \frac{v_{2n-1} - v_1''}{v_1'' + v_2''} \right\}. \quad \cdot \quad \cdot \quad (43)$$

Having regard to (40) and (41), and putting for shortness

$$v_{2n} - v_1'' = u_{2n}, \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (44)$$

we easily find

$$u_{2n} = D^{-1} B + \frac{D^{-2} (AD - BC)}{D^{-1} C + u_{2n-2}}, \quad \cdot \quad \cdot \quad \cdot \quad (45)$$

where

$$
\left.
\begin{aligned}
A &\equiv x'' (1-x')(v_1' - v_1'')(v_1'' + v_2')/(v_1' + v_2'), \\
B &\equiv x'' \{ v_1' - v_1'' + x' (v_1'' + v_2') \}/(v_1' + v_2'), \\
C &\equiv 1 - \frac{v_1' - v_1''}{v_1' + v_2'} (1-x') \left\{ 1 - \frac{(v_1'' + v_2')(1-x'')}{v_1'' + v_2''} \right\}, \\
D &\equiv \frac{1-x'}{v_1' + v_2'} + \frac{1-x''}{v_1'' + v_2''} - \frac{(v_1'' + v_2')(1-x')(1-x'')}{(v_1' + v_2')(v_1'' + v_2'')}.
\end{aligned}
\right\} \quad (46)
$$

Expressing each u with even suffix in terms of that with the next lowest suffix, we arrive at an expression for u_{2n} in terms of a continued fraction, viz.

$$u_{2n} = D^{-1} B + \frac{D^{-2}(AD - BC)}{D^{-1}(B + C) +} \quad \frac{D^{-2}(AD - BC)}{D^{-1}(B + C) + \ldots}. \quad (47)$$

All the elements are

$$D^{-2}(AD - BC) \div D^{-1}(B + C)$$

except the first and last, which are respectively

$$D^{-1} B \quad \text{and} \quad D^{-2}(AD - BC) \div \{ D^{-1} C + u_0 \}.$$

Similarly we can express

$$u_{2n-1} \equiv v_{2n-1} - v_1'$$

in terms of v_1 by means of a continued fraction, and v_1 is got from (40) by putting $n=1$.

After a large number of intervals T_1 and T_2 have succeeded each other, a species of steady state is reached in which the phenomena in successive intervals T_2 are practically identical, and the phenomena in successive intervals T_1 are practically identical. When this stage is reached we may in (45) take

$$u_{2n-2} = u_{2n},$$

and so find

$$u_{2n} \equiv v_{2n} - v_1'' = \frac{B-C}{2D} + \frac{\sqrt{(B-C)^2+4AD}}{2D}. \quad . \quad (48)$$

Similarly we should find

$$u_{2n-1} \equiv v_{2n-1} - v_1' = \frac{B'-C'}{2D'} + \frac{\sqrt{(B'-C')^2+4A'D'}}{2D'}, \quad (49)$$

where A', B', C', D' are derived from A, B, C, D respectively by interchanging v_1' with v_1'', v_2' with v_2'', T_1 with T_2, and so x' with x''.

The space actually travelled by the centres of the cups in a single double interval T_1+T_2 during this species of steady state is

$$s_{2n} + s_{2n+1} = v_1'T_1 + v_1''T_2 + \frac{1}{a_2}\log\left\{ 1 + \frac{v_{2n-1}-v_1''}{v_1''+v_2''}(1-x'') \right\}$$

$$+ \frac{1}{a_2}\log\left\{ 1 + \frac{v_{2n}-v_1'}{v_1'+v_2'}(1-x') \right\}, \quad (50)$$

where v_{2n} and v_{2n-1} are given by (48) and (49) for all possible circumstances of the kind under consideration.

The space which would be travelled on the equilibrium theory would be instead

$$v_1'T_1 + v_2''T_2.$$

The mean velocity in the final state is in reality

$$\bar{v} = (s_{2n+1}+s_{2n})/(T_1+T_2), \quad . \quad . \quad . \quad . \quad (51)$$

whereas on the equilibrium theory it would be

$$(v_1'T_1 + v_1''T_2)/(T_1+T_2).$$

In any individual case, supposing we knew the values of the constants appearing in (14), there would be no difficulty, except in the length of the arithmetical operations, in determining the error of the equilibrium mean velocity.

The most interesting case occurs when the alternations of

wind-velocity are rapid.   Supposing

$$a_2(v_1' + v_2')T_1 \quad \text{and} \quad a_2(v_1'' + v_2'')T_2$$

small, but n so large that

$$na_2(v_1' + v_2')T_1 \quad \text{and} \quad na_2(v_1'' + v_2'')T_2$$

are large, we find for the mean velocity in the final steady state,

$$\bar{v} \equiv (s_{2n} + s_{2n+1})/(T_1 + T_2)$$

$$= \frac{v_1'T_1 + v_1''T_2}{T_1 + T_2} + \frac{(v_1' + v_2')T_1 + (v_1'' + v_2'')T_2}{2(T_1 + T_2)}$$

$$\times \left[\left\{ 1 + \frac{4T_1 T_2(v_1' - v_1'')(v_2' - v_2'')}{((v_1' + v_2')T_1 + (v_1'' + v_2'')T_2)^2} \right\}^{\frac{1}{2}} - 1 \right]. \quad (52)$$

To deduce the true physical significance of (52) we must determine the sign of

$$(v_1' - v_1'')(v_2' - v_2'').$$

Now by (36) we have

$$v_2' - v_1' = (a_1 + 2b_2 V')/a_2,$$

$$v_2'' - v_1'' = (a_1 + 2b_2 V'')/a_2 ;$$

whence

$$v_2' - v_2'' = v_1' - v_1'' + \frac{2b_2}{a_2}(V' - V''). \quad . \quad . \quad (53)$$

Now the velocity of the cups in the steady state answering to a uniform wind is unquestionably greater the stronger the wind; thus $V' - V''$ and $v_1' - v_1''$ must have the same sign. Consequently, assuming b_2/a_2 positive, $(v_1' - v_1'')(v_2' - v_2'')$ has the same sign as $(v_1' - v_1'')^2$, or is necessarily positive.

Thus we see that (52) implies that, under the conditions supposed, whatever be the values of V'/V'' and T_1/T_2, the true mean velocity $\bar{v}$ of the cups is in excess of

$$(v_1'T_1 + v_1''T_2)/(T_1 + T_2),$$

the value given by the equilibrium theory.   The anemometer trace, interpreted in the usual way, thus exaggerates the mean velocity of the variable wind.   This exaggeration increases with $v_1' - v_1''$, and so with $V' - V''$.   The consequent error would thus be most serious during a gale in which violent gusts alternated with nearly calm intervals [*].

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[*] See an interesting paper by Mr. R. H. Curtis, Quart. Journ. Roy. Met. Soc. vol. xx. pp. 262 *et seq.*, especially pp. 266-7.

When $(V' \sim V'')/V'$ is small, then so likewise are

$$(v_1' \sim v_1'')/v_1' \quad \text{and} \quad (v_2' \sim v_2'')/v_2' ;$$

and (52) may be replaced by

$$\bar{v} = \frac{v_1' T_1 + v_1'' T_2}{T_1 + T_2} + \frac{T_1 T_2 (v_1' - v_1'')(v_2' - v_2'')}{(T_1 + T_2)\{(v_1' + v_2')T_1 + (v_1'' + v_2'')T_2\}}. \quad (54)$$

It is clear by (53) that $\bar{v}$ in this case differs from the mean velocity given by the equilibrium theory only by a term of the order $(V' - V'')^2/(V' + V'')$. Thus, if the fluctuations in the wind's velocity be small, we arrive at the same conclusion as in the different species of fluctuation treated in § 11, viz. that the error in the anemometer-record, treated as if the wind were steady, is very small.

Case $a_2 = 0$, V constant.

§ 15. As explained in § 9, experimental results obtained by Dr. Robinson have been deemed not inconsistent with the hypothesis that a_2 vanishes.

It is thus desirable to see the results we are led to when a_2 is supposed zero in the cases dealt with in §§ 13 and 14.

If V be constant throughout the time considered, then the solution (27) takes the form

$$v = \bar{v} + (v_0 - \bar{v})e^{-(a_1 + 2b_2 V)t}, \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (55)$$

where

$$\bar{v} = (c_2 V^2 - b_1 V - a_0)/(a_1 + 2b_2 V). \cdot \quad \cdot \quad (56)$$

We see from (55) how the influence of the initial velocity v_0 gradually dies out, and how v approaches the value $\bar{v}$, which is clearly the velocity of the cups in the steady state answering to the given wind-velocity V.

The size of c_2, the coefficient in the principal term in the driving-force, influences largely the value of $\bar{v}$, but has no direct influence on the rate at which the cups pick up their final velocity.

§ 16. We shall now examine what modifications the hypothesis $a_2 = 0$ introduces in the results when there are regular alternations of the wind's velocity, as in § 14.

Let v_0 be the initial value of v, and let $\bar{v}'$, $\bar{v}''$ be the velocities of the cups in steady states answering to the wind-velocities V' and V'' respectively. Use $v_1, v_2, \ldots v_{2n}, s_1 \ldots s_{2n}$, as in § 14, and for shortness let

$$\left. \begin{array}{l} e^{-\{(a_1 + 2b_2 V')T_1\}} = y', \\ e^{-\{(a_1 + 2b_2 V'')T_2\}} = y'', \end{array} \right\} \quad \cdot \quad \cdot \quad \cdot \quad (57)$$

Then we easily find

$$v_1 = \bar{v}' + (v_0 - \bar{v}')y',$$

$$\left.\begin{array}{l} v_{2n-1} = v_1(y'y'')^{n-1} + \dfrac{1-(y'y'')^{n-1}}{1-y'y''}\left\{\bar{v}'(1-y') + \bar{v}''y'(1-y'') \right\} \\[2mm] v_{2n} \;= v_0(y'y'')^n + \dfrac{1-(y'y'')^n}{1-y'y''}\left\{\bar{v}'y''(1-y') + \bar{v}''(1-y'')\right\}, \\[4mm] \qquad \cdot \qquad \cdot \qquad \cdot \qquad \cdot \qquad \cdot \qquad \cdot \qquad \cdot \qquad \cdot \\[3mm] s_{2n-1} = \bar{v}'\,\mathrm{T}_1 + (v_{2n-2} - v_{2n-1})/(a_1 + 2b_2\mathrm{V}'), \\[2mm] s_{2n} \;= \bar{v}''\mathrm{T}_2 + (v_{2n-1} - v_{2n})/(a_1 + 2b_2\mathrm{V}''). \end{array}\right\} \quad (58)$$

Let S be the whole space travelled by the centres of the cups in n double intervals $\mathrm{T}_1 + \mathrm{T}_2$. Then we find

$$S = \int_0^{n(\mathrm{T}_1+\mathrm{T}_2)} v\,dt$$

$$= n(\bar{v}'\mathrm{T}_1 + \bar{v}''\mathrm{T}_2) + (v_0 - v_{2n})/(a_1 + 2b_2\mathrm{V}')$$

$$+ \{v_1 + v_3 + \ldots + v_{2n-1}$$

$$- (v_2 + v_4 + \ldots + v_{2n})\}\left(\frac{1}{a_1 + 2b_2\mathrm{V}''} - \frac{1}{a_1 + 2b_2\mathrm{V}'}\right).$$

It is easy to prove

$$v_0 - v_{2n} = \{1-(y'y'') \}\left\{v_0 - \bar{v}' + (\bar{v}' - \bar{v}'')\frac{1-y''}{1-y'y''}\right\},$$

$$v_1 + v_3 + \ldots + v_{2n-1} - (v_2 + v_4 + \ldots + v_{2n})$$

$$= n\frac{(\bar{v}' - \bar{v}'')(1-y')(1-y'')}{1-y'y''}$$

$$+ y'\frac{(1-y'')\{1-(y'y'')^n\}}{1-y'y''}\left\{v_0 - \bar{v}' + (\bar{v}' - \bar{v}'')\frac{1-y''}{1-y'y''}\right\}$$

and, after some reductions, we find

$$S = n(\bar{v}'\mathrm{T}_1 + \bar{v}''\mathrm{T}_2) + n\frac{2b_2(\mathrm{V}' - \mathrm{V}'')(\bar{v}' - \bar{v}'')(1-y')(1-y'')}{(a_1 + 2b_2\mathrm{V}')(a_1 + 2b_2\mathrm{V}'')(1-y'y'')}$$

$$+ \left\{v_0 - \bar{v}' + (\bar{v}' - \bar{v}'')\frac{1-y''}{1-y'y''}\right\}\left\{\frac{1-(y'y'')^n}{a_1 + 2b_2\mathrm{V}'}\right\}$$

$$\times \left\{1 + \frac{2b_2(\mathrm{V}' - \mathrm{V}'')y'(1-y'')}{(a_1 + 2b_2\mathrm{V}'')(1-y'y'')}\right\}.$$

We may regard S as composed of three terms. The first term, $n(\bar{v}'\mathrm{T}_1 + \bar{v}''\mathrm{T}_2)$, would alone exist if the equilibrium theory were true; it is proportional of course to n. The

second term,

$$n \frac{2b_2(V'-V'')(\bar{v}'-\bar{v}'')(1-y')(1-y'')}{(a_1+2b_2V')(a_1+2b_2V'')(1-y'y'')},$$

also varies as n. The exponentials y', y'', $y'y''$ being necessarily less than unity, and the signs of $V'-V''$ and $\bar{v}'-\bar{v}''$ being, as explained in § 14, necessarily the same, this term is essentially positive. The third and remaining term does not contain n as a factor, and however much n is increased it cannot exceed an asymptotic value

$$\frac{1}{a_1+2b_2V'}\left\{v_0-\bar{v}'+(\bar{v}'-\bar{v}'')\frac{1-y''}{1-y'y''}\right\}\left\{1+\frac{2b_2(V'-V'')y'(1-y'')}{(a_1+2b_2V'')(1-y'y'')}\right\}.$$

Thus when a large number of double periods T_1+T_2 are considered we may to a close degree of approximation neglect the third term in S. We thus conclude that the total record from the anemometer is practically the same as if the cups had had a uniform velocity $\bar{v}$, given by

$$\bar{v}=\frac{\bar{v}'T_1+\bar{v}''T_2}{T_1+T_2}+\frac{2b_2(V'-V'')(\bar{v}'-\bar{v}'')(1-y')(1-y'')}{(T_1+T_2)(a_1+2b_2V')(a_1+2b_2V'')(1-y'y'')}, \quad (60)$$

where y', y'' are given by (57).

This result has been established for all values of

$$V':V'' \text{ and } T_1:T_2.$$

It leads to the same conclusion as § 14, viz., that the record from the anemometer, interpreted in the usual way, always exaggerates the wind's mean velocity when the actual velocity is variable.

When T_1 and T_2 are periods so short that $(a_1+2b_2V')T_1$ and $(a_1+2b_2V'')T_2$ are small, we deduce from (60) as a first approximation

$$\bar{v}=\frac{\bar{v}'T_1+\bar{v}''T_2}{T_1+T_2}+\frac{2b_2(V'-V'')(\bar{v}'-\bar{v}'')T_1T_2}{(T_1+T_2)\{(a_1+2b_2V')T_1+(a_1+2b_2V'')T_2\}}. \quad (61)$$

This result is easily shown to be in harmony with (52). The identification is simple when it is noticed that when a_2 becomes zero it is the root v_2 that becomes infinite. We take in (52)

$$v_2'/(a_1+2b_2V')=v_2''/(a_1+2b_2V''),$$

neglect v_1'/v_2', v_1''/v_2'', &c., and finally replace v_1' by $\bar{v}'$ and v_1'' by $\bar{v}''$.

Supposing V' and V'' given, and the conditions such that (61) applies, it is easily found for what value of T_1/T_2 the departure of $\bar{v}$ from the equilibrium value $(\bar{v}'T_1+\bar{v}''T_2)/(T_1+T_2)$ is greatest. We have only to make

$$T_2^{-1}(a_1+2b_2V')+T_1^{-1}(a_1+2b_2V'')$$

a minimum, regarding T_1+T_2 as a constant.

The result is

$$T_1/T_2 = \sqrt{\left(V'' + \frac{a_1}{2b_2}\right)\bigg/\left(V' + \frac{a_1}{2b_2}\right)}. \quad . \quad . \quad (62)$$

The interval during which the wind has the lower value should thus for the maximum effect be the greater.

When a_1 vanishes, or approximately in general when V' and V'' are both large compared to $a_1/2b_2$, (62) reduces to

$$T_1/T_2 = \sqrt{V''/V'}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (63)$$

§ 17. In §§ 14 & 16, T_1/T_2 and V'/V'' may both vary within wide limits, so that the conditions under which it has been proved that during a variable wind the cup-anemometer exaggerates the mean velocity are pretty comprehensive. It might still, however, be supposed that the result followed in some way from the restriction of there being only two velocities V' and V'', and evidence to the contrary is thus desirable.

The methods we have employed can be extended to apply to any number of different wind-velocities forming a regular sequence, but the work increases in length and the results in complexity as the number of intervals increases. I have thus worked out only one further case, where there are three intervals T_1, T_2, T_3, during which the wind's velocity has the respective values V', V'', V'''. As in § 16, we shall suppose a_2 zero.

$\bar{v}'''$ denotes the velocity of the cups in the steady state answering to V''', and

$$e^{-(a_1 + 2b_2 V''')T_3} = y'''.$$

Also for shortness,

$$(a_1 + 2b_2 V')^{-1} = C', \quad (a_1 + 2b_2 V'')^{-1} = C'', \quad (a_1 + 2b_2 V''')^{-1} = C'''.$$

The rest of the notation is as in § 16.

For the space S travelled by the cups' centres in the time $n(T_1 + T_2 + T_3)$, I find

$$S = n(\bar{v}'T_1 + \bar{v}''T_2 + \bar{v}'''T_3)$$

$$+ \frac{n}{1 - y'y''y'''}[(\bar{v}' - \bar{v}'')\{C''(1-y'') + C'''y''(1-y''') + C'y''y'''(1-y')\}$$

$$+ (\bar{v}'' - \bar{v}''')\{C'''(1-y''') + C'y'''(1-y') + C''y'''y'(1-y'')\}$$

$$+ (\bar{v}''' - \bar{v}')\{C'(1-y') + C''y'(1-y'') + C'''y'y''(1-y''')\}$$

$$+ \left[\frac{1-(y'y''y''')^n}{1-y'y''y'''}\right]\left\{v_0 - \bar{v}' + \frac{\bar{v}' - \bar{v}''' + y'''(\bar{v}''' - \bar{v}'') + y'''y''(\bar{v}'' - \bar{v}')}{1-y'y''y'''}\right.$$

$$\left. \times \{C'(1-y') + C''y'(1-y'') + C'''y'y''(1-y''')\}\right]. \quad . \quad (6$$

When n is large the expression inside the last square bracket cannot exceed the asymptotic value

$$\left\{ v_0 - \bar{v}' + \frac{\bar{v}' - \bar{v}''' + y'''(\bar{v}''' - \bar{v}'') + y'''y''(\bar{v}'' - \bar{v}')}{1 - y'y''y'''} \right\}$$
$$\times \frac{C'(1-y') + C''y'(1-y'') + C'''y'y''(1-y''')}{1 - y'y''y'''},$$

and thus is negligible compared to the first two expressions, which contain n as a factor. Omitting it, we have a comparatively simple formula for the mean velocity

$$\bar{v} = \frac{1}{n} S\ (T_1 + T_2 + T_3).$$

This formula, though probably the shortest for calculating the numerical value of $\bar{v}$ in a given case, is less convenient for the purpose of proving $\bar{v}$ in excess of the equilibrium value than is the following formula, deduced from it by algebraical manipulation :—

$$\bar{v}(T_1 + T_2 + T_3) - (\bar{v}'T_1 + \bar{v}''T_2 + \bar{v}'''T_3)$$

$$= \frac{2b_2}{1 - y'y''y'''} [C'C''(1-y')(1-y'')(V' - V'')(\bar{v}' - \bar{v}'')$$
$$+ C''C'''(1-y'')(1-y''')(V'' - V''')(\bar{v}'' - \bar{v}''')$$
$$+ C'''C'(1-y''')(1-y')(V''' - V')(\bar{v}''' - \bar{v}')]$$
$$+ \frac{(1-y')(1-y'')(1-y''')}{1 - y'y''y'''} [C'(\bar{v}' - \bar{v}'') + C''(\bar{v}'' - \bar{v}''')$$
$$+ C'''(\bar{v}''' - \bar{v}')].\ .\ (65)$$

Each of the three terms inside the first square bracket is, as seen in a similar case before, necessarily positive ; but one at least of the three terms inside the last square bracket is negative.

The subsequent proof depends on the exact circumstances of the case. Suppose for instance

$$V' > V'' > V''',$$

then put

$$C'(\bar{v}' - \bar{v}'') + C''(\bar{v}'' - \bar{v}''') + C'''(\bar{v}''' - \bar{v}')$$

$$= 2C'C''b_2(V' - V'')(\bar{v}'' - \bar{v}''') - 2C'C'''b_2(V''' - V')(\bar{v}''' - \bar{v}').$$

The first term of the two on the right is positive according to the hypothesis made. Now combine the second term with that one of the three terms in the first square bracket in (65)

which depends on $(V''' - V')(\bar{v}''' - \bar{v}')$, and there results the obviously positive expression

$$2b_2 C''' C' y''(1 - y''')(1 - y')(V''' - V')(\bar{v}''' - \bar{v}')/(1 - y'y''y''').$$

Thus on the hypothesis made as to the relative values of V', V'', V''', the right-hand side of (65) is essentially positive.

A similar proof will be found to apply whichever of the three V', V'', V''' is the greatest and whichever the least. Thus we reach the general result.

$$\bar{v} > (\bar{v}' T_1 + \bar{v}'' T_2 + \bar{v}''' T_3)/(T_1 + T_2 + T_3).$$

Summary.

The principal conclusions to which the formula (14) leads are as follows :—

1. In steady winds the ratio of the true wind-velocity to that of the cups may, in any given anemometer, be expected to be nearly constant when the wind is high. But there is no reason to expect this constancy when the wind is low, especially in cases where there is considerable friction owing to thickness in the lubricant or any other cause.

2. In steady winds the runs of two anemometers in which the friction is small may be expected to stand in a nearly constant ratio so long as the wind's velocity is considerable, but in light winds this constancy of ratio cannot be expected.

3. When the wind is not steady, changes in the velocity of the cups take place much more slowly than the changes in the wind's velocity to which they are due.

4. If the wind's velocity is nearly uniform, but has one or a series of small harmonic variations, the action of the cups is conspicuously to smooth down these variations when rapid, without introducing appreciable error into the estimate of the mean velocity.

5. If, however, the wind's velocity has large and frequent oscillations, the anemometer in addition to smoothing down the oscillations exaggerates the mean velocity. This exaggeration increases with the extent of the fluctuations ; it is greater in a case where the interval of time between successive gusts exceeds the duration of the gusts, than in a case where the converse occurs.

The formula (14) from which these conclusions flow is in part at least empirical. It is advanced provisionally, on the ground that as the prospect of a complete determination of the physical conditions of the problem and its satisfactory mathematical solution appears somewhat remote, it is desirable in the meantime to utilize the best existing data in such a way as to bring into stronger relief the issues which call for experimental investigation.

IV. *On the Use of an Iodine Voltameter for the Measurement of Small Currents.* By E. F. HERROUN, *F.I.C., Professor of Natural Philosophy, Queen's College, London*[*].

THE instruments in general use for the direct measurement of currents by electrolysis, as in the determination of reduction factors of galvanometers, comprise the hydrogen, silver, and copper voltameters : each of these possesses certain advantages, but none is free from defect. When occasion arises to make a large number of determinations of relatively small currents, the difficulties attending their use become more manifest.

Some of the defects of the ordinary types may be briefly stated. The hydrogen voltameter, consisting of platinum plates immersed in dilute sulphuric acid, has the following disadvantages :—

1. It acquires a large counter electromotive force of polarization, so that the current, on first joining up, is very inconstant.

2. Its internal resistance is subject to considerable fluctuations, according to the rate and mode of disengagement of the electrolytic gases.

3. Oxygen present in the dilute acid, or migrating from the anode, diminishes the amount of hydrogen collected, and so causes the current to be underestimated.

4. When small currents are being measured, the bubbles which cling to the electrodes or sides of the graduated tube cause an appreciable error.

5. Calculation of the current-strength is rendered difficult owing to the necessity for correcting the volume of gas for temperature, barometric pressure, and for the tension of vapour of the dilute acid employed, which last is frequently not exactly known.

In the silver voltameter the foregoing objections do not hold, with the exception of No. 3 ; for dissolved oxygen has been found to affect the yield of silver, a greater amount being obtained when the electrolysis is conducted *in vacuo* or hydrogen than in air. But in the silver voltameter the experimental difficulties in washing, drying, and weighing, it may be only a few centigrammes of silver, involve a large expenditure of time ; or if the weight of deposited silver be increased by prolonging the current, the difficulty of maintaining it constant is greater.

The difficulties which exist with silver are still more

apparent with copper ; for, as its chemical equivalent is much smaller, the weight of copper yielded by a given number of coulombs is only $\frac{31\cdot75}{108}$ of the weight of silver. In addition, its greater readiness to oxidize may cause the deposit of copper to become superficially oxidized in the process of washing and drying. This, however, may partly compensate for the defect in weight due to dissolved oxygen round the kathode.

If a list of the electrochemical equivalents of elements be examined, next to mercur*ous* mercury, the one which has the highest value will be found to be iodine ; and it is curious that, although the liberation of iodine from potassic iodide was very early used to detect electric currents, no attempt in recent years seems to have been made to utilize it for quantitative measurements.

As iodine is an anion, dissolved oxygen, which diminishes the yield at the kathode in other voltameters, will have no such action in a neutral solution of iodide ; and as its colour reaction with starch is extremely sharp, and its titration with standard sodium thiosulphate a process of greater accuracy than the performance of the average balance, the exact determination of the amount of iodine liberated by a current is both easy and rapid.

Experimental Details.

A voltameter consisting of platinum plates in a solution of potassic iodide is not suited for quantitative measurement ; as, upon electrolysis, it yields caustic potash and hydrogen at the kathode, the former of which by diffusion would come in contact with the iodine set free at the anode, converting it into iodide and iodate. If this were all it would be easy to acidify after electrolysis, when the iodine would be again set free ; but there is besides the additional disadvantage, that a rather large electromotive force of polarization is set up between the electrode surrounded by hydrogen and KOH and the one surrounded by iodine.

The solution actually employed was a 10 per cent. to 15 per cent. solution of neutral zinc iodide (a solution that keeps well if a small strip of zinc be suspended in it). The anode was a plate or disk of platinum placed at the bottom of a tall narrow beaker and joined by a platinum wire, sealed through a glass tube extending beyond the top of the beaker, to the outside circuit. In this way all the iodine is liberated at the bottom of the column of liquid, and, owing to its high density,

tends very little to diffuse upward. The kathode was a rod of amalgamated zinc, loosely jacketed with filter-paper or linen. The zinc rod should be supported so that it only dips a few centimetres into the top of the liquid, thus diminishing the liability of any of the liberated iodine coming in contact with it. The jacketing was found necessary to prevent particles of electro-deposited zinc becoming detached and falling into the solution of iodine at the bottom of the cell.

When used with currents not exceeding $\frac{1}{20}$ of an ampere and an anode of 9 square centimetres, it was found that no iodine diffused up to the level of the kathode in experiments of over an hour's duration, the cell being kept completely at rest. With feebler currents, lasting for a protracted time, it was found advisable to use a U-tube with a good plug of asbestos in the bend, filled with the zinc-iodide solution and having a platinum plate and zinc rod in the two sides of the tube ; but naturally with this form the resistance was much greater than with the beaker form.

With large currents " electric convection " leads to diffusion of the iodine through the whole liquid, and therefore the author does not consider it well adapted for their measurement, except for approximate, rapid determinations.

In the Report to the Board of Trade of the Electrical Standards Committee, the importance is pointed out, in using a silver voltameter, of having a considerable *wire*-resistance in the circuit to mitigate the effect of change of resistance in the voltameter itself : the same precautions apply to the iodine voltameter and a slight readjustment of the resistance at first employed is usually necessary to keep the current, as indicated by a galvanometer, constant. This is owing to a small change in the adverse electromotive force, but if a battery of fairly high E.M.F. (*ex. gr.* 3 Grove cells) be employed, controlled by a moderately large resistance, the current may be kept very constant.

After the iodine voltameter has been in circuit for a time which will vary with the degree of accuracy required and the actual strength of the current, the latter is stopped and the zinc kathode is immediately removed from the liquid. The solution is then stirred up, and the amount of free iodine determined by direct titration with standard sodium thiosulphate solution, after the addition of starch. Taking the electrochemical equivalent of iodine as ·001314 grm. per coulomb, a convenient strength of sodium thiosulphate solution is one of which each cubic centimetre reduces five times this amount (1 cub. centim. = ·00657 grm. I) : this corre-

sponds to a solution containing 12·845 grms. of pure sodium thiosulphate per litre; but it is necessary to standardize it from time to time with a standard solution of iodine, as its value is liable to change somewhat on keeping.

As pure zinc iodide is not always readily obtainable, though it can be easily prepared, the author has found that a solution of 15 per cent. zinc chloride, to which about 5 per cent. potassic iodide has been added, may be substituted for pure zinc iodide. Any chlorine, even if liberated, which is improbable with small current-densities, would at once yield its equivalent in iodine without escaping, and should any caustic potash form at the kathode it would merely produce zinc hydrate and potassic chloride.

A single example of the accuracy and rapidity of the method, selected from laboratory notes, may here be given :—

" Dec. 19, 1894.—Current through calibrated galvanometer = 20°.

> Time current was passing   = 2 hours.
>
> Weight of silver deposited = 0·2122 grm.
>
> Current (from above deposit) = 0·0264 ampere.

The same deflexion (20°) obtained using iodine voltameter.
Time = 30 minutes.

Iodine liberated required 9·6 cub. centim. of standard thiosul-phate sol. $9\cdot6 \times 5 = 48$ coulombs.   Current $= \dfrac{48}{1800^{\text{s}}} = 0\cdot0266$ amp."

The latter result is seen to be in fairly close agreement with that obtained with the silver voltameter, but slightly higher, as was to be expected from the reasons stated above. It will be noticed that the duration of the experiment was only a quarter of that with the silver voltameter.

In conclusion the points which recommend the iodine voltameter in the author's opinion are as follows :—

1. Its freedom from the effect of dissolved oxygen which gives " low " results with kationic voltameters.

2. The relatively short duration of the current necessary to obtain results of fair accuracy.

3. The rapidity of the volumetric estimation of the liberated iodine.

4. The ease and rapidity in calculating the results.

V. *Thermo-electric Powers of Metals and Alloys between the Temperatures of the Boiling-Point of Water and the Boiling-Point of Liquid Air. By* JAMES DEWAR, *LL.D., F.R.S., Professor of Chemistry in the Royal Institution, &c., and* J. A. FLEMING, *M.A., D.Sc., F.R.S., Professor of Electrical Engineering in University College, London, &c.**

[Plates III. & IV.]

1. IF one junction of a thermo-electric couple is at a temperature $t°$, and if the two junctions of the couple differ in temperature by a very small interval dt, and if the electromotive force of the couple under these conditions is dE, then the *thermo-electric power* of the couple at the temperature $t°$, denoted by P, is defined by the relation

$$P = \frac{dE}{dt}.$$

The well-known thermo-electric diagram of Professor Tait embodies the results of his own investigations on the thermo-electric powers of metals within the limits of the temperatures which can be reached by mercury thermometers and certain temperatures above this range. Starting from the facts first made known by Lord Kelvin in his classical thermo-dynamical researches, Professor Tait showed that on certain assumptions the curves representing thermo-electric power plotted as a function of temperature should be straight lines, and consequently that the lines of thermo-electromotive force obtained by plotting as ordinates the electromotive force in a thermo-electric circuit of two metals, one junction of which is kept at a constant temperature, whilst the temperature of the other junction is varied, should be parabolas with their axes vertical if plotted in terms of the variable temperature as abscissæ. Experiment within the above-mentioned range of temperature confirmed these conjectures for a large number of thermo-couples, but led to the remarkable discovery that the thermo-electric lines of certain metals—notably of the magnetic metals, nickel and iron—are, for temperatures above zero Centigrade, broken lines characterized by sudden changes of direction. This thermo-electric diagram of Professor Tait exhibits in a very elegant manner the chief thermo-electric facts, and enables the temperature of inversion to be determined by inspection.

2. Having it in our power to carry down the temperature

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* Communicated by the Authors.

of a thermo-electric junction to values in the neighbour-
hood of −200° C. by the employment of considerable quan-
tities of boiling liquid air and liquid oxygen, we have been
able to conduct an extensive investigation on the thermo-
electric powers of metals at temperatures lying between this
low temperature and that of the boiling-point of water;
and have been thus enabled to continue the thermo-electric
diagram down to temperatures not very far removed from
the absolute zero.   We have accordingly been able to
determine the points of electric inversion which lie between
0° C. and −200° C., and to compare these observed values
with those predicted by the extrapolation of the existing
thermo-electric diagram of Professor Tait obtained from
observations at higher limits of temperature.   The chief
interest, however, attaching to these investigations was the
ability to determine whether, over these wide limits of low
temperature, the thermo-electric lines of various metals
remain straight lines, and whether any of the metals exhibit
changes of thermo-electric power at low temperatures which
cause their thermo-electric lines to be bent or broken—
thus indicating a sudden change in the sign or magnitude of
the "Thomson effect" at certain temperatures.   The results
of these experiments have been set out in a chart of thermo-
electromotive forces of the various metals and alloys used in
conjunction with pure lead as a thermo-couple, and from which
all the required information can be obtained.   This chart and
the details of observations below provide the data for a full
discussion of these questions.

3. The metals used by us in this investigation were for the
most part in the form of wires, and were in many cases taken
from the samples of pure metals employed by us in a series of
determinations of the specific electrical resistance of metals at
low temperature[*].   Omitting as unnecessary an account of
much preliminary investigation, we proceed to describe the
final experimental arrangements as follows :—

A large number of thermo-electric couples were prepared,
each consisting of two wires of lead joined by an intermediate
wire of another metal M.   The lead wire was prepared by
pressing pure lead into a wire ·0656 centim. in diameter, and
the other metallic wires had diameters approximately from
about ·025 to ·15 centim., or else were used in the form of
very thin narrow strips.   The lead wires had a length of
50 centimetres, and the connecting wire of the metal or alloy

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[*] See Dewar and Fleming, "The Electrical Resistance of Metals and
Alloys at Temperatures approaching the Absolute Zero," Phil. Mag.
September 1893, p. 271.

M a length of about 54 centimetres. The junctions of each couple having been carefully soldered together, each wire was covered over with paraffined silk ribbon so as to insulate it, leaving only one junction exposed. A number of these thermo-couples were made up into a bundle, the sets of bare and covered junctions being bound together compactly, the bare in one group and the insulated junctions in another. In all the experiments to be described, the set of junctions which were insulated was kept at 0° C. by being immersed in finely-crushed melting ice, kept well drained ; the other set of junctions was exposed to temperatures ranging from −200° C. to +100° C. Two measurements had then to be made, viz., that of the temperature of the heated or cooled junction and also that of the electromotive force set up in the corresponding thermo-couple by the difference of temperature of the two junctions. The chief experimental difficulty encountered was that of determining the low temperature and determining it at the instant when the electromotive-force measurement of the couple was made. After long preliminary experiments necessary to overcome obstacles in the path, the successful method of dealing with the problem was found. These difficulties arose almost entirely out of the fact that for our purpose it was not sufficient to determine the thermo-electromotive force of the M−lead couple at fixed isolated temperatures, but we desired to determine it at any of the intermediate points of temperature lying within the range of three hundred degrees from −200° C. to +100° C. over which we were working. The apparatus finally constructed was based upon the employment of a platinum thermometer of particular form for measuring the temperature, and a measuring-instrument which could be changed instantly from a potentiometer into a resistance-balance.

4. In our previous researches on electric conductivity at low temperature, we fully satisfied ourselves that a wire of carefully annealed pure soft platinum can be cooled as often as necessary to the temperature of boiling liquid air or oxygen and yet return always to the same electrical resistance at a normal standard temperature.

Professor Callendar has demonstrated that this quality of the constancy of resistance of pure annealed platinum at determined temperatures renders it admirably adapted for thermometric purposes ; and Callendar and Griffiths have shown that a properly arranged platinum resistance affords the most suitable means for determining temperatures, and our own work at low temperatures has confirmed this fact. In our investigations on the electrical resistance of metals and alloys,

we gave all our temperature-measurements in *platinum tem-peratures*, as defined by one standard platinum thermometer; and all the measurements in this present thermo-electric research are given in terms of the same standard platinum thermometer, which we shall hereafter mention as our standard platinum thermometer P_1.

If at any time it becomes necessary, these temperatures can be reduced to other scales of measurement.

For several reasons it was necessary to construct a platinum thermometer of special form for this thermo-electric work; and this was made as follows:—A small cylinder or tube of copper 3·2 centim. long, and having a longitudinal hole through it ·64 centim. in diameter, was wrapped round with two other half-cylinders of copper. These half-cylinders had bevelled edges. One half-cylinder was soldered to the central tube, and the other half-cylinder was insulated from the tube and from the first half-cylinder by a slip of mica. The whole was formed into a fairly true cylinder on the outside. Two wires of platinoid No. 18 s.w.g. and 30 centim. long were then soldered to the two insulated half-cylinders. These platinoid wires were kept apart by distance-pieces of ebonite. A thin sheet of mica was then wrapped round the cylinder, and over this was wound 100 centim. of pure annealed silk-covered platinum wire. One end of this wire was soldered to one copper half-cylinder, and the other end to the second insulated half. It will thus be seen that we had a platinum wire connecting the ends of the platinoid wires but wound on a highly conducting copper cylinder, the over-all diameter of the bobbin being about a centimetre and a quarter. This wire constituted the platinum thermometer which will hereafter be spoken of as the working thermometer. A section and elevation of the thermometer is given in Pl. III. fig. 1. To the ends of the platinoid wires were soldered long stranded and well-insulated flexible copper connecting leads. A duplicate was then constructed in exactly the same manner, save that it had no platinum wire but had the two copper half-cylinders connected metallically together. The object of constructing this duplicate was to be able to eliminate from all measurements the resistance of the platinoid and copper wires forming the connectors of the platinum thermometer wire.

Our platinum thermometer consisted therefore of a platinum wire and of connecting conductors partly of platinoid and partly of stranded copper wire, and a blank or duplicate composed of a loop of an identical platinoid and copper wire. The reason for interposing the platinoid wire was as follows. As will be seen presently, our method of procedure to obtain

temperatures intermediate between fixed and known temperatures, such as that of the boiling-point of liquid oxygen and the mixture of solid carbonic acid and ether, was to embed the thermo-junctions in a mass of paraffin wax, and this mass having been cooled down to about −200°, was allowed very slowly to heat up again.

If a platinum thermometer with copper leading-in wires is immersed in this way in paraffin wax, to determine the temperature of the junctions, then, as the thermal conductivity of the copper is greatly increased by cooling it, heat will very rapidly flow into the thermometer along the leading-in wires; and it was found by preliminary experiments quite impossible under these conditions to keep the temperature of the platinum wire used as a thermometer down to the same temperature as the thermo-junction in contact with it. By employing an alloy like platinoid of a rather high specific resistance, and by making the cross section of these platinoid leading wires relatively somewhat small, it was found possible to greatly hinder the passage of heat along the legs of the thermometer, and yet by the employment of an identical blank conducting circuit to determine the exact temperature of the platinum wire itself from its measured resistance.

Returning, then, to the construction of the thermometer, we may mention that it was constructed of a length of platinum wire given to one of us by Professor Callendar, and that this specimen was remarkable for its relatively large temperature-coefficient. In order to determine the resistance, and therefore the temperature, of this platinum thermometer, a slide-wire bridge was constructed. A length of two metres of uniformly drawn manganin wire was stretched over a two-metre scale. This wire constituted the bridge slide-wire. It had a diameter of ·0193 centim. (No. 36 s.w.g.) and a resistance at 15° C. of 26·576 ohms. It was very carefully calibrated for resistance per unit of length. Over this slide-wire moved a contact-maker; and the other two arms of the bridge consisted of a coil of manganin wire wound on a small bobbin and having a resistance of 5·000 ohms at 15° C., and the above-described platinum thermometer or the resistance representing its leading-in wires. The battery employed with the bridge was a two-cell lithanode secondary battery, and the galvanometer a Holden-Pitkin suspended-coil galvanometer of 4 ohms resistance. Battery- and galvanometer-keys were inserted in the circuits as usual.

The first step in the investigation consisted in determining the resistance of the platinum thermometer attached to this bridge, which we shall speak of as the working thermometer P_2, at temperatures defined by our standard platinum thermo-

H 2

meter P_1.   These platinum temperatures it may be mentioned
are defined as follows :—A platinum wire has its resistance
determined at 0° C. and 100° C., correction being made for
the resistance of its own leading-in wires.   A horizontal
line on a chart is then taken to represent temperature on the
platinum scale and ordinates are set up at distances represented
by 100 divisions on this horizontal line, and these ordinates
made proportional in length to the true resistance R_0 and R_{100}
of the standard platinum wire at 0° C. and 100° C. respec-
tively.   Through the summit of these ordinates a straight
line is then drawn, and the point where it cuts the horizontal
axis of temperature is the absolute zero of temperature by
that wire.   The platinum temperature of any other body, say
of boiling liquid oxygen, is then obtained by measuring the
resistance of the standard platinum wire immersed in this
medium, and after correcting for the resistance of the leading-
in wires, obtaining the true resistance R of the standard wire
in the liquid oxygen.   On looking out on the chart the vertical
ordinate, which to the selected scale represents this resistance,
it will indicate by its abscissa the platinum temperature *pt*
by that thermometer of the boiling liquid oxygen.   For our
standard thermometer P_1 the absolute zero is $-283°\cdot0$ plati-
num degrees on the above-described scale of temperature.

The coefficients and absolute zero-points of the
thermometers P_1 and P_2 are as follows :—

The constants of our standard platinum thermometer P_1 are:—

R_0 =resistance of platinum wire at 0° C. =3·1059 ohms.
R_{100} =resistance of platinum wire at 100° C.=4·2034 ohms.
R   =resistance at any platinum temperature *pt*.
pt   =platinum temperature as defined by the equation

$$pt = 100\,\frac{R-R_0}{R_{100}-R}.$$

The resistance R at any platinum temperature as defined
by this thermometer is given by the equation

$$R = \cdot010975\,(pt + 283\cdot0).$$

α=mean temperature-coefficient between 0° C. and 100° C.
=·003534.

$$\alpha = \frac{R_{100}-R_0}{100\,R_0}.$$

$-\dfrac{1}{\alpha}$=reciprocal of temperature-coefficient$= -283°\cdot0$.

The absolute zero of this wire is $-283°\cdot0$ in terms of its own
platinum temperature.

The platinum temperature pt (measured from melting-point of ice) is obtained from R, the resistance at $pt°$, by the equation

$$pt = 91 \cdot 12\,R - 283 \cdot 0.$$

The platinum temperature of solid carbonic acid melting in ether at 760 mm. is $-81 \cdot 9$ platinum degrees by this thermometer; and the platinum temperature of liquid oxygen boiling at 760 mm. is $-196 \cdot 7$ platinum degrees by this thermometer.

The constants of our working thermometer P_2 are:—

R_0 = resistance at $0°$ C. = $7 \cdot 303$ ohms.

R_{100} = resistance at $100°$ C. = $10 \cdot 140$ ohms.

α = mean temperature-coefficient between $0°$ C. and $100°$ C. = $\cdot 003885$.

$-\dfrac{1}{\alpha} = -257° \cdot 42.$

The absolute zero of this wire is $-283° \cdot 0$ in terms of its own platinum temperature.

Platinum temperature as measured by this thermometer is given by the equation

$$pt = 35 \cdot 25\,R - 257 \cdot 42,$$

where R is the resistance of the wire at $pt°$.

The platinum temperature of solid carbonic acid in ether at 760 mm. is $-81° \cdot 3$ platinum degrees by this thermometer; and the platinum temperature of liquid oxygen boiling under 760 millim. is $-193° \cdot 3$ platinum degrees by this thermometer.

We find that the number representing the platinum temperature of liquid oxygen boiling under 760 mm. when taken by the working platinum thermometer P_2 is not quite identical with that given by the standard platinum thermometer P_1. Into the cause of this we will not now stop to enquire, because it did not interfere at all with our use of the working thermometer P_2. Having determined the resistance of the working platinum thermometer and of the standard platinum thermometer when immersed together in boiling liquid oxygen, solid carbonic acid and ether, melting ice ($0°$ C.), and boiling water ($100°$ C.), we were able to construct a curve which gave us the true platinum temperature in terms of our standard platinum thermometer P_1 of the working platinum thermometer P_2 when immersed in any medium which gave it a definite resistance, and hence a definite point of balance on the slide-wire of the bridge. In order to shorten the labour of correcting the observations, a scale was constructed which enabled us to infer by inspection at once from the actual

slide-wire reading the temperature of our working thermometer P_2 in terms of our standard platinum thermometer P_1, all corrections for connexions being included. Hence, when the working thermometer P_2 is immersed in any liquid or region of sufficiently constant or slowly varying temperature, and when the position of balance of the contact on the slide-wire is found so that the resistance-bridge is balanced, then we know from this scale at once the platinum temperature of the wire of our working thermometer in terms of our standard platinum thermometer. This bridge and thermometer has proved of the very greatest use, since it enables us to measure instantly any temperatures between absolute zero and something approaching to 200° C., which is the highest our working thermometer will bear without injury. As an instance of the degree of accuracy in temperature measurement we can obtain with this instrument, we may mention that in the neighbourhood of $-196°\cdot7$, which is the platinum temperature of boiling liquid oxygen, we can with ease distinguish a change of temperature of one twenty-fifth of a degree. The same degree of accuracy is not obtained at all temperatures; but the temperatures between 0° C. and 100° C. can be determined to within one tenth of a degree with ease.

The above arrangements therefore enabled us to instantly determine the temperature of the platinum wire of our working thermometer, and therefore, when the temperature was constant or very slowly varying, to determine the temperature of the hollow copper cylinder on which the working platinum wire was wound.

5. The set of bare junctions of the thermo-couples prepared as described above was then inserted into the hollow interior of the little copper cylinder of the working thermometer, and kept tightly pressed against the copper by a small conical wooden peg. We satisfied ourselves by experiment that under these conditions, if the temperature of the region in which the copper cylinder was placed was constant or very slowly varying, the temperature of the platinum wire wound round the copper cylinder was the same as that of the junctions packed into the interior of the cylinder. This being the case, we had at once the means of determining the temperature of the junctions by means of one measurement, made instantly, of the resistance of the platinum wire. We have next to describe the arrangements for determining the thermo-electromotive force set up in the couples when one set of junctions was kept at 0° C., and the other varied.

This was accomplished by the employment of a potentiometer

arrangement (see Pl. III. fig. 2). The calibrated manganin wire used for the resistance-balance serves also as a potentiometer wire, and the same secondary battery and galvanometer by a different arrangement of connexions are employed to complete the potentiometer. A platinoid resistance of 18,200 ohms was constructed, and also a set of four coils of manganin wire of the same diameter as the bridge wire were prepared, and the whole of these coils joined in series with the bare manganin wire stretched over the scale. These four coils had resistances respectively equal to one, two, three, and four times that of the bridge slide-wire. We then constructed an arrangement by which we could use the same slide wire either as a bridge to measure the resistance of the working platinum thermometer, and hence to determine the temperature of the junctions inside it, or to measure the electromotive force set up in the thermo-couple by balancing it against a variable standard potential-difference calibrated with reference to a Clark cell.

It was necessary to make provision for changing the bridge into a potentiometer very rapidly, and for the purpose the connexions of the different parts of the apparatus were arranged as shown in Pl. III. fig. 2, so that by one movement of a double copper connecting-piece the connexions of the apparatus could be instantly changed from a bridge to measure the temperature of the thermometer, to a potentiometer to measure the electromotive force of the thermo-couple. The whole of the electromotive-force measurements are therefore referred to a Clark cell.

The arrangement of the combined bridge and potentiometer may be described a little more in detail as follows, and will be easily understood by reference to the diagram in Pl. III. fig. 2.

XZWY is the two-metre slide-wire having its ends attached to terminal blocks X and Y. B is the two-cell battery which is connected through the current-reverser D with the ends of the slide-wire, having interposed between one terminal and the block Y either a resistance R_2 of about 200 ohms, when used as a bridge, or resistance R_1, R_4, and R_3 when used as a potentiometer. R_1 was a variable resistance of about or up to 5000 ohms; R_4 was a resistance of 18,200 ohms; and R_3 a resistance of $10 \times 25 \cdot 576$ ohms divided into four sections having ratios of 1, 2, 3, and 4 in magnitude. The galvanometer G was connected to terminals U and V when used as a bridge, and P was the slide contact on the wire; the other two arms consisted of the platinum thermometer P_1 joined in between n and o and the 5-ohm coil C joined in between l and m. When used as a potentiometer, the thermo-couple Th

of which the electromotive force was being measured was connected in series with the galvanometer, and joined in between the slider P and the end of the resistance R_4.　In this case the fall of potential down the slide-wire was measured as usual by a Clark cell Ck.　In order to make the changes of connexion rapidly from bridge to potentiometer, a seven-cup mercury switch S was employed, so that by shifting a pair of copper forks all the necessary changes of connexion were made instantly.

6. The operations of measurement were then as follows :—

One set of the thermo-junctions being immersed in melting ice, the working thermometer, with the other set of thermo-junctions packed inside it, was placed in a small copper tube closed at the bottom end, not touching the tube, and this was filled full of melted paraffin-wax.　The copper tube was then placed in a test-tube and the whole filled with melted paraffin-wax, to between the copper tube and the glass test-tube.　When the wax was solid, the mass containing the thermometer-wire and junctions enclosed within it was cooled down by the employment of considerable quantities of liquid air to a temperature of about $-200°$.　As soon as the temperature had become constant, the mass of paraffin was lifted out and placed in a vacuum-jacketed vessel that it might become heated up by conduction and radiation very slowly. A series of observations was then taken for each junction in rotation, measuring first the temperature of the junctions by the thermometer-wire resistance, then changing the connexions, and measuring the electromotive force of the couple, then changing back again to the bridge arrangement to get the temperature of the junction again; and so on for each couple in rotation, as the mass of paraffin slowly warmed up.　In this manner a series of observations was obtained which, when reduced, gave the electromotive force of the couple in absolute C.G.S. units and the standard platinum temperature (pt) of the variable junction at that instant, the other junction being kept at $0°$ C. all the time.

By the employment of carbonic acid and ether and a paraffin-oil bath the series of observations for closely adjacent temperatures was continued for each thermo-couple from the boiling-point of liquid air up to the boiling-point of water. In addition to this, very careful observations were taken of the E.M.F. of all the couples at fixed stationary temperatures, such as that of the boiling-point of liquid oxygen, the melting-point of solid carbonic acid, the melting-point of ice, and the boiling-point of pure water, and the intermediate observations were made in some cases with the temperature of the junctions

rising, and in some cases falling, to give assurance that the temperature of the platinum wire was the same as that of the junctions, and did not lag behind it. Satisfactory evidence was obtained that the temperature of the platinum wire did truly represent the temperature of the thermo-junction buried in the interior of the thermometer.

We were thus enabled to obtain a series of numbers for each metal, representing at defined temperatures the thermo-electromotive force of that metal against lead. Having still in our possession a small quantity of exceedingly pure lead prepared in M. Stas's laboratory which was kindly given to us by Mr. George Matthey for our previous resistance experiments, we were enabled to measure the thermo-electromotive force of a couple formed of this pure Stas's lead and the ordinary lead used by us as the associated metal for all the couples. It was thus possible to reduce all our observations of thermo-electromotive force to a statement of the electromotive force in C.G.S. units of a couple formed of a metal M and of chemically pure lead, one junction being at $0°$ C., and the other being at a platinum temperature pt as defined by our standard platinum thermometer P_1. In the following Tables the results of all the corrected observations are given, and graphically shown plotted down in the chart (see Plate IV.).

These lines of thermo-electromotive force thus found in terms of platinum temperature are in all cases curved lines. Wherever the curve has a maximum point so that its tangent becomes parallel to the line taken as the axis of temperature, the temperature at which this occurs is the neutral point of that metal or alloy with regard to lead. If at any temperature the tangents of the curves of two metals are parallel to one another, that temperature is the neutral point of those two metals with regard to each other, or is the temperature of inversion.

The diagram of thermo-electric powers can be at once obtained from that of the thermo-electromotive forces by drawing a series of lines, the ordinates of which represent to a proper scale the *slope* of the curves of thermo-electromotive force.

With regard to the purity of the metals employed in this research, we may mention that the samples of platinum, gold, silver, palladium, copper, tin, lead, cadmium, magnesium, nickel (Mr. Mond's nickel deposited from nickel carbonyl), zinc, and aluminium were either the same wires as were used by us in our investigation on specific resistance, or were of

equal purity. The antimony and bismuth were prepared for us by Mr. George Matthey, to whom our thanks are especially due for valuable assistance in this matter. The other alloys used were taken as found in commerce. The iron was a sample of the softest annealed transformer iron obtainable. As regards the manganese-steel, two samples of Hadfield's 12-per-cent. manganese-steel were used, one in its ordinary non-magnetic condition, and one of the same composition but which had been rendered sensibly magnetic by heating it to a full red-heat. It will be seen that this operation quite appreciably alters its thermo-electric value. The carbon used was a carbon filament from an incandescent lamp.

In the following Tables the values of the electromotive force of a thermo-couple formed of the metal and two chemically pure lead wires are given in C.G.S. units, as determined from a particular Clark cell, for stated temperatures. The sign + before the value of the E.M.F. signifies that the lead wire in connexion with that end of the metal which is at 0° C. is higher in potential than the other lead wire ; and the sign — that the reverse is the case. The curves in the appended chart are plotted from these tables.

No. 1.

Platinum-Lead Couple.

One junction at 0° C.; the other at $pt°$.

E.M.F. of Couple in C.G.S. units.	Temperature $pt°$ in degrees of Standard Platinum Thermometer.	E.M.F. of Couple in C.G.S. units.	Temperature $pt°$ in degrees of Standard Platinum Thermometer.
−29630	+ 99·9	+ 1090	− 6·0
−25370	+ 90·3	+ 1530	− 9·8
−21920	+ 81·2	+ 2800	− 21·9
−18200	+ 71·0	+ 4530	− 38·9
−14670	+ 61·1	+ 4980	− 56·7
−11750	+ 51·0	+ 4750	− 64·9
− 8910	+ 41·7	+ 4150	− 80·7
− 8850	+ 41·0	+ 3520	− 90·2
− 6830	+ 33·2	+ 1010	−109·3
− 4920	+ 25·4	− 4150	−135·1
− 4760	+ 24·6	−12040	−161·1
− 2830	+ 15·6	−19220	−181·0
− 2810	+ 15·5	−24690	−192·8
− 2050	+ 12·3	−26590	−196·3
− 2080	+ 11·6	−30930	−205·6

No. 2.

Platinum-Lead Couple.   (Callendar's Platinum Wire.)

One junction at 0° C.; the other at $pt°$.

E.M.F. of Couple in C.G.S. units.	Temperature $pt°$ in degrees of Standard Platinum Thermometer.	E.M.F. of Couple in C.G.S. units.	Temperature $pt°$ in degrees of Standard Platinum Thermometer.
−43550	+ 100·2	+ 9610	− 44·1
−38530	+ 91·0	+10810	− 53·0
−34950	+ 83·7	+11910	− 62·4
−29320	+ 73·7	+12370	− 72·2
−24840	+ 64·3	+12770	− 81·1
−20360	+ 54·5	+12540	− 91·6
−16440	+ 45·5	+11820	−105·8
−11550	+ 34·3	+ 9090	−122·9
− 8130	+ 24·7	+ 5670	−137·8
− 5270	+ 16·5	+ 2280	−151·9
− 4740	+ 15·5	− 1490	−164·5
− 2650	+ 9·0	− 7470	−178·8
+ 1740	− 6·4	−10810	−188·0
+ 4620	− 16·2	−16140	−195·5
+ 7060	− 28·0		

No. 3.

Gold-Lead Couple.

One junction at 0° C.; the other at $pt°$.

E.M.F. of Couple in C.G.S. units.	Temperature $pt°$ in degrees of Standard Platinum Thermometer.	E.M.F. of Couple in C.G.S. units.	Temperature $pt°$ in degrees of Standard Platinum Thermometer.
+11600	+ 99·9	− 830	− 7·1
+10330	+ 90·2	− 840	− 8·5
+ 9090	+ 81·0	− 2020	− 21·3
+ 7670	+ 70·8	− 3340	− 37·7
+ 6675	+ 60·5	− 4970	− 55·8
+ 5380	+ 51·0	− 5680	− 65·4
+ 4430	+ 41·6	− 6940	− 80·8
+ 3820	+ 39·9	− 7370	− 89·0
+ 3440	+ 33·2	− 8690	−108·1
+ 2340	+ 25·1	−10160	−134·1
+ 2260	+ 24·4	−11560	−159·8
+ 1510	+ 15·8	−12420	−180·7
+ 1390	+ 15·5	−13020	−192·7
+ 1360	+ 12·3	−13040	−196·3
+ 940	+ 10·9	−13420	−205·4

No. 4.

Palladium-Lead Couple.

One junction at 0° C.; the other at *pt*°.

E.M.F. of Couple in C.G.S. units.	Temperature *pt*° in degrees of Standard Platinum Thermometer.	E.M.F. of Couple in C.G.S. units.	Temperature *pt*° in degrees of Standard Platinum Thermometer.
−90920	+100·1	+33010	− 55·6
−79810	+ 90·1	+37640	− 65·6
−70570	+ 80·7	+43810	− 80·9
−59380	+ 70·6	+45730	− 88·0
−50220	+ 60·4	+50270	−107·1
−41210	+ 51·0	+51900	−121·0
−32680	+ 41·6	+53830	−132·1
−29960	+ 38·7	+53980	−137·4
−25680	+ 33·3	+54140	−138·0
−18030	+ 24·6	+54170	−138·7
−17970	+ 24·3	+54230	−139·6
−11380	+ 15·9	+53840	−151·0
−11200	+ 15·4	+53520	−153·1
− 9140	+ 12·3	+53380	−154·8
− 7450	+ 10·3	+52660	−158·0
+ 5480	− 7·1	+49360	−179·6
+ 5610	− 7·8	+45650	−191·6
+13630	− 21·0	+44530	−196·4
+23740	− 36·9	+41110	−205·0

No. 5.

Silver-Lead Couple.

One junction at 0° C.; the other at *pt*°.

E.M.F. of Couple in C.G.S. units.	Temperature *pt*° in degrees of Standard Platinum Thermometer.	E.M.F. of Couple in C.G.S. units.	Temperature *pt*° in degrees of Standard Platinum Thermometer.
+33200	+100·1	− 2050	− 6·5
+29140	+ 90·0	− 2650	− 8·5
+26090	+ 81·2	− 5630	− 20·1
+22100	+ 70·5	− 9630	− 36·0
+18960	+ 60·6	−14590	− 54·7
+15490	+ 51·1	−17580	− 65·9
+12410	+ 41·5	−21060	− 80·9
+10970	+ 38·0	−22260	− 86·7
+ 9820	+ 33·3	−26150	−105·8
+ 6730	+ 24·2	−31250	−130·6
+ 6400	+ 23·9	−35520	−156·6
+ 4460	+ 16·0	−39270	−178·9
+ 4270	+ 15·4	−41260	−190·6
+ 3860	+ 12·3	−42060	−196·4
+ 2210	+ 9·4	−43400	−205·0

No. 6.

Copper-Lead Couple.

One junction at 0° C.; the other at $pt°$.

E.M.F. of Couple in C.G.S. units.	Temperature $pt°$ in degrees of Standard Platinum Thermometer.	E.M.F. of Couple in C.G.S. units.	Temperature $pt°$ in degrees of Standard Platinum Thermometer.
+31590	+100·1	− 1770	− 5·9
+27520	+ 89·9	− 2630	− 9·1
+24500	+ 81·6	− 5070	− 19·7
+20860	+ 70·4	− 8830	− 35·2
+17850	+ 61·0	−13130	− 53·6
+14320	+ 51·6	−15970	− 66·5
+11540	+ 41·3	−19240	− 80·8
+10060	+ 37·3	−20300	− 85·9
+ 9120	+ 33·3	−24180	−104·7
+ 6200	+ 24·1	−28550	−129·9
+ 5780	+ 23·0	−32980	−155·2
+ 4190	+ 16·1	−36620	−178·7
+ 3880	+ 15·3	−38320	−189·9
+ 3610	+ 12·3	−40050	−196·3
+ 1985	+ 8·8	−39920	−196·4
		−41350	−205·1

No. 7.

Zinc-Lead Couple.

One junction at 0° C.; the other at $pt°$.

E.M.F. of Couple in C.G.S. units.	Temperature $pt°$ in degrees of Standard Platinum Thermometer.	E.M.F. of Couple in C.G.S. units.	Temperature $pt°$ in degrees of Standard Platinum Thermometer.
+32390	+100·2	− 810	− 3·3
+28060	+ 89·9	− 2600	− 10·7
+24360	+ 80·4	− 4500	− 18·4
+20920	+ 70·4	− 7840	− 33·8
+17970	+ 61·1	−11700	− 51·9
+14100	+ 50·4	−14220	− 66·2
+11100	+ 41·2	−17130	− 80·6
+ 9260	+ 35·9	−18100	− 84·8
+ 8880	+ 33·2	−21140	−102·9
+ 6180	+ 24·3	−24640	−127·4
+ 5140	+ 21·4	−27540	−152·1
+ 4270	+ 16·1	−30910	−176·6
+ 3780	+ 15·3	−31900	−188·4
+ 3450	+ 12·4	−32140	−196·4
+ 1620	+ 7·5	−33000	−204·8

No. 8.

Cadmium-Lead Couple.

One junction at 0° C.; the other at *pt*°.

E.M.F. of Couple in C.G.S. units.	Temperature *pt*° in degrees of Standard Platinum Thermometer.	E.M.F. of Couple in C.G.S. units.	Temperature *pt*° in degrees of Standard Platinum Thermometer.
+48020	+100·2	− 1180	− 4·0
+40940	+ 89·9	− 2900	− 9·9
+35480	+ 81·1	− 5120	− 19·1
+29370	+ 70·3	− 8560	− 34·6
+24600	+ 61·2	−12140	− 52·6
+19380	+ 50·6	−14290	− 66·4
+15030	+ 41·2	−16350	− 80·7
+12810	+ 36·6	−17200	− 85·2
+11560	+ 33·3	−19340	−103·8
+ 7920	+ 24·1	−21450	−128·8
+ 7000	+ 22·1	−23410	−153·8
+ 5160	+ 16·1	−25330	−178·0
+ 4680	+ 15·3	−26090	−189·1
+ 4330	+ 12·4	−26460	−196·4
+ 2220	+ 8·1	−26940	−205·0

No. 9.

Magnesium-Lead Couple.

One junction at 0° C.; the other at *pt*°.

E.M.F. of Couple in C.G.S. units.	Temperature *pt*° in degrees of Standard Platinum Thermometer.	E.M.F. of Couple in C.G.S. units.	Temperature *pt*° in degrees of Standard Platinum Thermometer.
−1260	+100·1	+ 1110	− 44·8
−1210	+ 90·3	+ 1310	− 53·5
−1150	+ 84·3	+ 1830	− 63·2
− 960	+ 74·2	+ 2160	− 72·4
− 800	+ 64·2	+ 2530	− 81·1
− 760	+ 55·6	+ 3180	− 89·6
− 780	+ 45·1	+ 3900	−104·2
− 610	+ 34·1	+ 4910	−121·2
− 340	+ 24·1	+ 5910	−136·4
− 190	+ 16·5	+ 7160	−152·7
− 190	+ 15·5	+ 8210	−165·7
− 230	+ 9·0	+ 9430	−178·7
+ 60	− 5·9	+ 9990	−183·8
+ 280	− 14·8	+11330	−195·5
+ 600	− 28·1		

No. 10.

Tin-Lead Couple.

One junction at 0° C.; the other at *pt°*.

E.M.F. of Couple in C.G.S. units.	Temperature *pt°* in degrees of Standard Platinum Thermometer.	E.M.F. of Couple in C.G.S. units.	Temperature *pt°* in degrees of Standard Platinum Thermometer.
+570	+100·1	0	− 2·0
+460	+ 89·9	− 80	− 11·7
+410	+ 79·4	− 50	− 16·7
+360	+ 70·1	−140	− 31·6
+340	+ 60·7	−150	− 48·7
+340	+ 50·5	−240	− 64·2
+270	+ 41·2	−290	− 80·8
+190	+ 33·6	−220	− 81·8
+200	+ 33·1	−260	−100·9
+140	+ 25·2	−360	−124·2
+150	+ 19·6	−340	−147·8
+ 90	+ 16·2	−440	−168·6
+ 80	+ 15·2	−430	−185·8
+ 50	+ 12·4	−490	−196·4
+ 70	+ 6·1	−440	−203·8

No. 11.

Iron-Lead Couple.

One junction at 0° C.; the other at *pt°*.

E.M.F. of Couple in C.G.S. units.	Temperature *pt°* in degrees of Standard Platinum Thermometer.	E.M.F. of Couple in C.G.S. units.	Temperature *pt°* in degrees of Standard Platinum Thermometer.
+145360	+100·1	− 2840	− 1·1
+132110	+ 89·9	− 20030	− 12·1
+117540	+ 79·2	− 26240	− 15·9
+104830	+ 69·9	− 49090	− 30·4
+ 91940	+ 60·4	− 76050	− 46·7
+ 77150	+ 50·8	−104190	− 64·0
+ 61930	+ 41·3	−131940	− 80·0
+ 50780	+ 33·1	−134250	− 80·9
+ 47990	+ 32·5	−163590	− 99·8
+ 39180	+ 25·9	−201010	−122·5
+ 27680	+ 19·0	−235730	−146·1
+ 24380	+ 16·3	−264340	−168·1
+ 23300	+ 15·2	−286090	−185·7
+ 20870	+ 12·4	−298860	−196·3
+ 7120	+ 5·5	−305400	−203·9

No. 12.

Nickel-Lead Couple.

One junction at 0° C.; the other at *pt*°.

E.M.F. of Couple in C.G.S. units.	Temperature *pt*° in degrees of Standard Platinum Thermometer.	E.M.F. of Couple in C.G.S. units.	Temperature *pt*° in degrees of Standard Platinum Thermometer.
− 188860	+ 100·1	+ 60180	− 41·1
− 158380	+ 86·3	+ 72990	− 50·1
− 150070	+ 82·1	+ 84490	− 59·1
− 130890	+ 72·8	+ 94230	− 67·0
− 110810	+ 62·6	+ 109470	− 80·9
− 95400	+ 54·5	+ 112400	− 83·8
− 85430	+ 49·2	+ 126290	− 97·6
− 57140	+ 33·8	+ 141470	− 112·9
− 45770	+ 27·1	+ 156090	− 130·0
− 26740	+ 16·5	+ 171260	− 149·7
− 25530	+ 15·7	+ 178190	− 160·7
− 14790	+ 9·2	+ 187180	− 175·9
+ 14110	− 9·0	+ 189730	− 181·5
+ 27570	− 18·3	+ 198040	− 195·5
+ 42520	− 28·5		

No. 13.

Pianoforte Steel-Lead Couple.

One junction at 0° C.; the other at *pt*°.

E.M.F. of Couple in C.G.S. units.	Temperature *pt*° in degrees of Standard Platinum Thermometer.	E.M.F. of Couple in C.G.S. units.	Temperature *pt*° in degrees of Standard Platinum Thermometer.
+ 96030	+ 100·1	− 1460	− 0·8
+ 87140	+ 89·9	− 12920	− 12·2
+ 77200	+ 79·1	− 16100	− 15·3
+ 68730	+ 70·3	− 30680	− 29·6
+ 59260	+ 60·2	− 47310	− 46·0
+ 50250	+ 50·8	− 65250	− 63·7
+ 40480	+ 41·2	− 81810	− 79·3
+ 32890	+ 33·0	− 84660	− 80·8
+ 30290	+ 31·8	− 101240	− 98·7
+ 26040	+ 26·2	− 124030	− 120·5
+ 17330	+ 18·4	− 145180	− 144·6
+ 15900	+ 16·3	− 163340	− 167·1
+ 15000	+ 15·2	− 177260	− 185·6
+ 13310	+ 12·4	− 184770	− 196·3
+ 4220	+ 5·1	− 189650	− 204·0

No. 14.

Hadfield's Manganese Steel-Lead Couple.   (Non-Magnetic.)

One junction at 0° C.; the other at $pt°$.

E.M.F. of Couple in C.G.S. units.	Temperature $pt°$ in degrees of Standard Platinum Thermometer.	E.M.F. of Couple in C.G.S. units.	Temperature $pt°$ in degrees of Standard Platinum Thermometer.
−57360	+100·1	+ 320	− 0·3
−51120	+ 89·9	+ 6700	− 12·4
−44700	+ 79·1	+ 8060	− 14·8
−40320	+ 71·3	+15360	− 28·7
−33280	+ 60·1	+23840	− 44·9
−27870	+ 50·7	+32260	− 62·4
−22190	+ 41·2	+40590	− 78·0
−17930	+ 33·0	+42300	− 80·8
−16570	+ 31·1	+49850	− 97·0
−14290	+ 26·2	+58960	−116·7
− 9040	+ 17·9	+71110	−142·7
− 8730	+ 16·4	+80480	−166·0
− 8060	+ 15·2	+88100	−184·4
− 6840	+ 12·5	+92770	−196·0
− 2410	+ 4·9	+95260	−203·5

No. 15.

Hadfield's Manganese Steel-Lead Couple.   (Magnetic.)

One junction at 0° C.; the other at $pt°$.

E.M.F. of Couple in C.G.S. units.	Temperature $pt°$ in degrees of Standard Platinum Thermometer.	E.M.F. of Couple in C.G.S. units.	Temperature $pt°$ in degrees of Standard Platinum Thermometer.
−52190	+100·0	+17570	− 37·2
−51160	+ 96·9	+22580	− 49·0
−42360	+ 82·9	+27360	− 59·6
−36860	+ 72·6	+30190	− 65·5
−32290	+ 63·3	+36900	− 80·0
−26950	+ 53·2	+37740	− 81·1
−24160	+ 47·8	+42980	− 94·1
−17150	+ 34·3	+49190	−108·7
−13900	+ 27·3	+56440	−127·0
− 8040	+ 16·4	+64170	−147·0
− 7840	+ 16·0	+68330	−157·2
− 4720	+ 9·4	+74680	−174·0
+ 4240	− 9·7	+77500	−182·0
+ 9350	− 20·7	+81680	−195·5
+13610	− 29·5		

No. 16. Manganin-Lead Couple.

One junction at 0° C.; the other at $pt°$.

E.M.F. of Couple in C.G.S. units.	Temperature $pt°$ in degrees of Standard Platinum Thermometer.	E.M.F. of Couple in C.G.S. units.	Temperature $pt°$ in degrees of Standard Platinum Thermometer.
+13770	+100·1	− 4950	− 60·9
+12220	+ 89·9	− 5200	− 64·1
+11000	+ 79·7	− 5600	− 68·0
+ 9200	+ 72·1	− 5830	− 72·6
+ 7520	+ 60·1	− 5900	− 74·1
+ 6300	+ 50 5	− 5850	− 76·2
+ 5240	+ 41·2	− 6350	− 78·0
+ 4080	+ 32·7	− 6210 }	− 80·7
+ 3130	+ 29·1	− 6360 }	
+ 3115	+ 26·2	− 6570	− 81·7
+ 1760	+ 16·5	− 6560	− 83·5
+ 1670	+ 16·1	− 6670	− 85·7
+ 1750	+ 15·3	− 7150	− 88·6
+ 2070	+ 12·6	− 7190	− 92·9
+ 550	+ 3·9	− 7450	− 93 0
+ 290	+ 1·1	− 7690	− 99·4
− 1010	− 12·7	− 8000	−105·4
− 1060	− 13·0	− 8550	−110·4
− 2510	− 26·4	−- 8540	−112·2
− 3460	− 41·0	−10010	−137·5
− 3790	− 42·4	−11040	−160·4
− 3790	− 44·5	−12850	−182·5
− 4320	− 54·1	−13490	−196·2
− 4660	− 57·7	−14130	−203·1
− 5320	− 60·2		

No. 17. German Silver-Lead Couple.

One junction at 0° C.; the other at $pt°$.

E.M.F. of Couple in C.G.S. units.	Temperature $pt°$ in degrees of Standard Platinum Thermometer.	E.M.F. of Couple in C.G.S. units.	Temperature $pt°$ in degrees of Standard Platinum Thermometer.
−125050	+100·1	+ 320	− 0·1
−110490	+ 89·9	+ 13070	− 12·4
− 95650	+ 79·2	+ 14790	− 14·1
− 85890	+ 72·0	+ 28390	− 27·7
− 69920	+ 60·0	+ 43170	− 43·8
− 57530	+ 50·6	+ 58180	− 61·0
− 45940	+ 41·2	+ 70910	− 76·4
− 36440	+ 32·9	+ 74030	− 80·7
− 32260	+ 30·4	+ 85250	−- 95·5
− 28820	+ 26·2	+ 97580	−115·2
− 17810	+ 17·1	+113170	−140·4
− 17340	+ 16·4	+124670	−162·4
− 16220	+ 15·2	+133830	−183·1
− 13570	+ 12·5	+139270	−196·0
− 3910	+ 4·5	+139540	−196·0
		+141950	−203·1

No. 18.

Platinoid-Lead Couple.

One junction at 0° C.; the other at $pt°$.

E.M.F. of Couple in C.G.S. units.	Temperature $pt°$ in degrees of Standard Platinum Thermometer.	E.M.F. of Couple in C.G.S. units.	Temperature $pt°$ in degrees of Standard Platinum Thermometer.
− 120250	+ 100·1	+ 30	− 0·5
− 105970	+ 89·9	+ 13290	− 12·6
− 92550	+ 79·4	+ 14230	− 13·4
− 82620	+ 72·2	+ 27200	− 26·9
− 66570	+ 60·0	+ 41680	− 42·9
− 54690	+ 50·5	+ 57060	− 60·4
− 44080	+ 41·2	+ 69980	− 75·1
− 34720	+ 32·8	+ 73810	− 80·7
− 30680	+ 29·8	+ 83450	− 93·9
− 27710	+ 26·2	+ 96950	− 113·1
− 15850	+ 16·6	+ 112560	− 138·6
− 16690	+ 16·5	+ 125160	− 161·0
− 15540	+ 15·3	+ 134770	− 182·7
− 12940	+ 12·5	+ 141120	− 196·0
− 3500	+ 4·2	+ 143760	− 202·9

No. 19.

(Pure) Bismuth-Lead Couple.

One junction at 0° C.; the other at $pt°$.

E.M.F. of Couple in C.G.S. units.	Temperature $pt°$ in degrees of Standard Platinum Thermometer.	E.M.F. of Couple in C.G.S. units.	Temperature $pt°$ in degrees of Standard Platinum Thermometer.
−754480	+98·1	+ 301840	− 38·5
−673080	+87·2	+ 379590	− 49·0
−590550	+75·9	+ 506570	− 65·6
−573490	+74·2	+ 578310	− 77·2
−479360	+60·9	+ 623330	− 83·7
−398360	+50·7	+ 744280	− 99·1
−317540	+40·0	+ 869260	− 122·2
−208380	+26·1	+ 952840	− 140·1
−153740	+20·1	+ 1006770	− 152·0
− 59940	+ 8·5	+ 1074700	− 165·1
+ 69530	− 7·5	+ 1125800	− 181·6
+153990	−18·5	+ 1178210	− 195·7
+212970	−26·5		

I 2

No. 20.

(Commercial) Bismuth-Lead Couple. (No. 1.)

One junction at $0°$ C.; the other at $pt°$.

E.M.F. of Couple in C.G.S. units.	Temperature $pt°$ in degrees of Standard Platinum Thermometer.	E.M.F. of Couple in C.G.S. units.	Temperature $pt°$ in degrees of Standard Platinum Thermometer.
− 579100	+ 100·1	+ 64580	− 44·4
− 539720	+ 94·3	+ 63600	− 52·1
− 458330	+ 84·0	Balancing position variable.	
− 388860	+ 74·0	+ 52480	− 64·2
− 334700	+ 66·3	Balancing position variable.	
− 272930	+ 55·9	+ 47810	− 70·8
− 212460	+ 46·2	+ 33120	− 81·0
− 152140	+ 34·2	+ 29640	− 87·9
− 100400	+ 24·1	+ 2700	− 102·2
− 66460	+ 16·5	− 35570	− 119·5
− 64720	+ 15·6	− 70960	− 135·2
− 43120	+ 9·8	− 105760	− 153·3
− 40720	+ 9·1	− 130870	− 165·3
+ 11870	− 7·0	− 159240	− 178·7
+ 27780	− 14·8	− 167740	− 186·9
+ 53090	− 28·5	− 187370	− 195·5

No. 21.

(Commercial) Bismuth-Lead Couple. (No. 2.)

One junction at $0°$ C.; the other at $pt°$.

E.M.F. of Couple in C.G.S. units.	Temperature pt^c in degrees of Standard Platinum Thermometer.	E.M.F. of Couple in C.G.S. units.	Temperature $pt°$ in degrees of Standard Platinum Thermometer.
− 664150	+ 100·0	+ 113070	− 28·4
− 612480	+ 92·4	+ 153140	− 43·0
− 533680	+ 83·0	+ 168800	− 51·0
− 457460	+ 73·2	+ 184340	− 61·6
− 388400	+ 63·2	+ 189780	− 68·9
− 329450	+ 55·0	+ 190120	− 81·0
− 287060	+ 48·8	+ 201840	− 85·8
− 191070	+ 33·9	+ 200110	− 99·7
− 136130	+ 25·9	+ 192340	− 115·0
− 86090	+ 16·5	+ 174830	− 132·6
− 80600	+ 15·6	+ 153910	− 152·0
− 47690	+ 9·7	+ 140310	− 163·2
− 45050	+ 9·1	+ 117460	− 177·4
+ 37150	− 8·2	+ 108890	− 184·7
+ 70020	− 16·2	+ 87350	− 195·5

No. 22.

Antimony-Lead Couple.

One junction at 0° C. ; the other at *pt*°.

E.M.F. of Couple in C.G.S. units.	Temperature *pt*° in degrees of Standard Platinum Thermometer.	E.M.F. of Couple in C.G.S. units.	Temperature *pt*° in degrees of Standard Platinum Thermometer.
+31560	+ 98·3	− 810	− 35·3
+25800	+ 88·0	− 440	− 46·9
+18920	+ 74·9	+ 110	− 60·4
+13200	+ 60·1	+ 1960	− 81·8
+ 9820	+ 50·5	+ 3180	− 96·0
+ 6990	+ 39·5	+ 6280	−121·7
+ 3950	+ 26·6	+ 8360	−140·5
+ 2790	+ 20·1	+ 9970	−153·6
+ 1030	+ 8·1	+10930	−162·8
− 160	− 5·6	+12900	−180·4
− 760	− 17·0	+13990	−195·7
− 960	− 24·4		

No. 23.

Aluminium-Lead Couple.

One junction at 0° C. ; the other at *pt*°.

E.M.F. of Couple in C.G.S. units.	Temperature *pt*° in degrees of Standard Platinum Thermometer.	E.M.F. of Couple in C.G.S. units.	Temperature *pt*° in degrees of Standard Platinum Thermometer.
− 3940	+100·0	+ 2300	− 39·4
− 3650	+ 93·3	+ 2690	− 49·5
− 3260	+ 82·1	+ 3350	− 58·9
− 2990	+ 72·4	+ 4040	− 66·2
− 2730	+ 62·8	+ 5240	− 81·1
− 2250	+ 53·7	+ 5250	− 81·8
− 2070	+ 48·2	+ 6520	− 96·1
− 1430	+ 33·9	+ 7910	−111·0
− 1100	+ 27·3	+ 9400	−128·6
− 560	+ 16·5	+11360	−148·0
− 610	+ 15·8	+12410	−159·2
− 410	+ 9·3	+14530	−175·0
+ 380	− 9·5	+15150	−181·4
+ 1020	− 19·8	+17420	−195·5
+ 1440	− 29·0		

No. 24

Carbon-Lead Couple.

One junction at 0° C. ; the other at $pt°$.

E.M.F. of Couple in C.G.S. units.	Temperature $pt°$ in degrees of Standard Platinum Thermometer.	E.M.F. of Couple in C.G.S. units.	Temperature $pt°$ in degrees of Standard Platinum Thermometer.
+127950	+ 98·2	− 34400	− 33·3
+109830	+ 85·9	− 46070	− 44·9
+ 97840	+ 77·0	− 59360	− 58 6
+ 74550	+ 60·1	− 77750	− 79·7
+ 62110	+ 50·7	− 89560	− 93·9
+ 46980	+ 38·9	−109880	−121·6
+ 31560	+ 26·3	−122030	−140·6
+ 22690	+ 20·1	−129490	−152·5
+ 10510	+ 9·0	−132770	−161·8
− 3210	− 4·3	−141460	−179·4
− 14630	− 14·7	−149480	−196·2
− 23780	− 23·0		

We propose to reserve for a future communication a full discussion of the interpretation of these curves and the bearing of the facts they disclose on the usually accepted thermo-electric theory. Meanwhile it may be sufficient to note that none of these thermo-electric curves are true parabolas over their whole extent. Many of the curves as drawn in the chart in Plate IV. are curves of double curvature, and in some cases point to the existence of more than one neutral point with lead. We propose to convert this chart of electromotive forces into a chart of thermo-electric powers, in which last condition it will lend itself better to a discussion of results. A few remarks may, however, be made respecting the thermo-electromotive force curves shown in the chart. The lines of iron and pianoforte-steel, as well as some others, have changes of curvature at certain points which indicate that the thermo-electric lines are broken lines. The line of antimony has two points at which its tangent becomes parallel to the line of lead, indicating that the thermo-electric line of antimony cuts that of lead twice. The bismuth lines are very peculiar. The curves marked Bismuth No. 1 and Bismuth No. 2 are specimens of impure or commercial bismuth ; but both these and the curve of pure bismuth have a sudden break or discontinuity in their course at about −80°, which we think is not due to errors

of experiment. These and many other points are receiving consideration, and will be discussed in a subsequent communication. We must, in conclusion, express our great obligations to Mr. D. K. Morris, as well as to Mr. C. Jakeman, for the valuable assistance they have rendered to us in the laborious work of taking and reducing the observations above recorded, as well as in the construction of some of the apparatus used in this research.

VI. *Experimental Proof of* Van't Hoff's *Constant, of* Arrhénius's *Generalization, and of* Ostwald's *Law of Dilution in very Dilute Solutions.* *By* Dr. MEYER WILDERMANN * .

I. *Proof of* Van't Hoff's *Constant.*

IT is well known that it was Van't Hoff who first drew attention to the fact that the equations representing the generalizations arrived at by Boyle, Gay-Lussac, and Avogadro in the case of gases are equally applicable to dissolved substances, if the osmotic pressure of the molecules of the dissolved substance be substituted for the pressure of the gas.

Van't Hoff deduced these laws for solution from thermodynamical considerations—a method which gives them increased validity,—and illustrated them from the osmotic experiments of Pfeffer and de Vries.

At the same time Van't Hoff was able to establish a thermodynamical relation between the osmotic pressure of a dissolved substance and the molecular lowering of vapour-pressure; molecular lowering of freezing-point of the solution thereby furnishing a rational basis for the empirical generalizations of Raoult and of Babo and Wüllner, who had previously investigated the same point.

In Van't Hoff's thermodynamical argument the solutions are assumed to be very dilute, and hence their experimental verification is specially important for the case of very dilute solutions.

The determination of the molecular depression of the freezing-point is the safest and most convenient method of testing the validity of these generalizations, and this has been done for moderately dilute solutions by Van't Hoff himself

and by Ejkman ; and the equation

$$t = \frac{0 \cdot 02 \, T^2}{w},$$

where T=absolute temperature, w=latent heat of fusion of the solvent, has been experimentally verified and confirmed for several solvents.

The method of determining the freezing-point of very dilute solutions[*], which was devised by my late friend P. B. Lewis, from 0° to −0°·2, and my recent investigations of similar solutions from −0°·2 to −0°·4 and of the freezing-point of water [†], have given us a means of submitting Van't Hoff's equation,

$$t = \frac{0 \cdot 02 \, T^2}{w},$$

to a more accurate verification.

The value of t is 1·87 if, with Bunsen and others, we take the latent heat of water to be 80 cal., and is somewhat greater if w is put = 79·6 cal.

First come the experimental data.   In the following Tables α is the number of molecules in solution per litre (in pure water this is 0) ; γ is the freezing-point of the water or of the solution, as read on the $\frac{1}{1000}°$ thermometer ; δ the number of readings of the temperature made after the freezing-point has been reached ; ϵ the limits within which the readings of the temperature varied ; ϕ is the time over which the readings extended ; b is the amount of over-cooling, or difference between the temperature of the solution before and after the formation of ice, these temperatures being read on the $\frac{1}{100}°$ thermometer ; c, the temperature of the ice-bath ; c', the temperature of the room ; k is the reading of the barometer.

* See 'Transactions of the Chemical Society,' 1894.   A fuller account has been given in the *Zeitschrift für phys. Chemie*, xv. p. 358.   See also the very valuable work of Jones, *Zeitschr. phys. Chemie*, xi. p. 110.   Later investigations of Jones have shown that his method was not brought to the high development we all supposed.   It is now a long time ago since Professor Ostwald told me that it is also his opinion that the method used by Jones requires a further development, because the results obtained for non-electrolytes by this method do not agree with the fundamental generalizations of the modern Theory of Solutions.   The work of Lewis, which is distinguished by great experimental accuracy, and by the minute and judicious care with which the conditions necessary to secure the best possible results are investigated, enables us now to submit many important questions in very dilute solutions to a more accurate verification.

† See *Zeitschr. phys. Chemie*, xv. p. 365.

Table I. (1/1000° thermometer.)

Cane-sugar.

a.	γ.	δ.	ε.	φ.	b.	c.	c'.	k.
								millim.
0 *	·4858(9)	5	·4858–·4859	10		−1·8 to −2	18	756·5
0 *	·4857(8)	7	·4857–·4858	10		−1·8 to −2	18	756·3
0 †	·4873(4)		......	...			...	756·3
0·006535 ‡	·4758(7)	5	·4758–·4757	8		−1·8 to −2	18	756·5
0·019344 ‡	·4514(3)	4	·4514–·4513	8		−1·8 to −2	18	757·5
0·03164 †	·4279(8)	7	·4279–·4277	10		−2	18·2	757·5
0·04344 ‡	·4067(6)	7	·4066–·4068	10		−2	18·3	757·5
0·05477 ‡	·3848(9)	7	·3847–·3849	10		−2	17·5	760·5
0·06565 ‡	·3634	9	·3633–·3635	10		−2	17·3	760·5
0·07609 ‡	·3428(9)	6	·3427–·3429	10		−2	17·1	760·5
0·08612 ‡	·3233(4)	6	·3233–·3234	10		−2	17	760·5

Urea.

a.	γ.	δ.	ε.	φ.	b.	c.	c'.	k.
0 *	·4851(2)	8	·4850–·4852	9		−1·7	20	760·65
0 *	·4852	7	·4852–·4853	8		−1·8 to −2	19	760·5
0 †	·4867(8)	...	......	...		......	...	760·5
0·001813 ‡	·4819	7	·4819–·4820	8		−1·8	18	760·5
0·00905 ‡	·4694	5	·4694–·4692	5		−2	18·5	760·4
0·02341 ‡	·4427(8)	6	·4628–·4628	9		−1·8	18·5	760·5
0 *	·4852(3)	6	·4851–·4853	12		−2	19·7	759·5
0·043506 ‡	·4026(7)	6	·4026–·4027	9		−1·8	19·3	759·5
0·07802 ‡	·3355(6)	6	·3355–·3358	7		−1·8	19·1	759·5
0·11116 ‡	·2687(8)	8	·2685–·2688	12		−2	19	759·5

Alcohol, C_2H_5OH.

a.	γ.	δ.	ε.	φ.	b.	c.	c'.	k.
0 *	·4844(5)	7	·4845–·4854	10		−1·8	15·6	754·2
0 †	·4860(1)	...	......	...		......	...	754·2
0·00645 ‡	·4738	7	·4737–·4739	8		−1·8	15	754·2
0·01930 ‡	·4510(1)	5	·4510–·4512	8		−2	14	754·5
0·04495 ‡	·4033	9	·4032–·4034	12		−2	13·8	754·8
0·09582 ‡	·3086	9	·3085–·3087	12		−2	13·5	754·8
0·1459 ‡	·2152	6	·2152–·2151	10		−2	13·5	754·8
0 *	·4848(7)	6	·4848–·4847	10		−1·8 to −2	15·5	753·7
0·1548 ‡	·1985	9	·1984–·1986	10		−2	15·5	753·7
0·2039 ‡	·1064	6	·1063–·1065	12		−1·8 to −2	15·3	753·6
0·2039 ‡	·1063(4)	6	·1063–·1064	9		−2	15·2	753·7

* Ice-cap on the bulb of the thermometer.
† Ditto, corrected by +0°·0016.
‡ No ice-cap is formed on the Hg bulb of the thermometer.

From these experimental data are deduced the following Tables, in which are given :—

α, the number of molecules of the substance dissolved, p. litre.

a, the lowering of the freezing-point which is observed.

b, the number of degrees of over-cooling read on the smaller thermometer.

c, the amount of the solvent which separated as ice, expressed in percentages.

d, the factor by which the number of molecules given under α must be multiplied in order to obtain

α corrected ; *i. e.* the concentration of the solution after the separation of the ice. (It is better to correct the density than the lowering of the freezing-point, on account of dissociation.)

$\dfrac{a}{\alpha\ \text{corrected}}$ gives the molecular lowering of the freezing-point, which, according to Van't Hoff, is represented by

$$t = \frac{0\cdot02\text{T}^2}{w} = 1\cdot878 \ (\text{if } w = 79\cdot6),$$

or $\qquad\qquad = 1\cdot87 \quad (\text{if } w = 80).$

TABLE II.

Cane-sugar.						
α mol. norm.	*a.*	*b.*	*c.*	*d.*	α corr.	$\beta = \dfrac{a}{\alpha\ \text{corr.}} \times 100$
(1.) 0·006535	[0·0100(1)] 0·016(7)	0·888	per cent. 1·06	$\frac{100}{98\cdot94}$	0·006602	[151·5] 175·7 (177·2)
(2.) 0·019344	[0·0344(5)] 0·0360(1)	0·855	1·03	$\frac{100}{98\cdot97}$	0·019546	[176 (176·5)] 184·5 (184·7)
(3.) 0·03164	[0·0579(80)] 0·0595(6)	0·731	0·88	$\frac{100}{99\cdot12}$	0·03192	[181·4 (181·7)] 186·4 (186·7)
(4.) 0·04344	[0·0792(1)] 0·0808(9)	0·789	0·95	$\frac{100}{99\cdot05}$	0·04386	[180·6 (180·3)] 184·3 (184·5)
(5.) 0·05477	[0·1010(1)] 0·1026(7)	0·755	0·91	$\frac{100}{99\cdot09}$	0·05527	[182·7 (182·9)] 185·6 (185·8)
(6.) 0·06565	[0·1224] 0·1240(1)	0·673	0·81	$\frac{100}{99\cdot19}$	0·06619	[184·9] 187·3 (187·5)
(7.) 0·07609	[0·1430(1)] 0·1446(7·8)	0·751	0·90	$\frac{100}{99\cdot1}$	0·07678	[186·2 (186·4)] 188·3 (188·5)
(8.) 0·08612	[0·1624(5)] 0·1640(1)	0·643	0·77	$\frac{100}{99\cdot25}$	0·08679	[187·1 (187·3)] 189·0 (189·1)

Urea.

a mol. norm.	a.	b.	c.	d.	a corr.	$\beta = \dfrac{a}{a \text{ corr.}} \times 100$
(1.) 0·001813 *	0·0034(3)	0·862	per cent. 1·03	$\dfrac{100}{98\cdot97}$	0·001832	*185·6 (181·2)*
(2.) 0·00905	[0·0158] 0·0174(3)	0·850	1·02	$\dfrac{100}{98\cdot98}$	0·009142	[172·8] *195·8 (189·2)*
(3.) 0·02341	[0·0424(5)] 0 0440(1)	0·804	0·96	$\dfrac{100}{99\cdot04}$	0·02364	[179·4 (179·8)] *186·1 (186·6)*
(4.) 0·04351	[0·0826] 0 0842	0·68	0·82	$\dfrac{100}{99\cdot18}$	0·04387	[188·3] *191·8*
(5.) 0·07803	[0·1497] 0·1513	0·67	0·81	$\dfrac{100}{99\cdot19}$	0·07866	[190·3] *192·4*
(6.) 0·1112	[0·2165] 0 2181	0·585	0·70	$\dfrac{100}{99\cdot3}$	0·1120	[193·3] *194·7*

Alcohol, C_2H_5OH.

a mol. norm.	a.	b.	c.	d.	a corr.	$\beta = \dfrac{a}{a \text{ corr.}} \times 100$
(1.) 0·00645	[0·0106(7)] 0 0122(3)	0·94	per cent. 1·18	$\dfrac{100}{98\cdot82}$	0·006527	[162·4 (163·9)] *186·9 (188·4)*
(2.) 0·01930	[0·0337] 0·0353	0·975	1·22	$\dfrac{100}{98\cdot78}$	0·01953	[172·6] *180·8*
(3.) 0·04495	[0·0811(2)] 0·0827(8)	0·933	1·166	$\dfrac{100}{98\cdot83}$	0·04548	[178·3 (178·5)] *(182·1) 181·8*
(4.) 0·09582	[0·1758(9)] 0·1774(5)	0·87	1·09	$\dfrac{100}{98\cdot91}$	0·09688	[181·5 (181·6)] *(183·3) 183·1*
(5.) 0·1459	[0·2692(3)] 0·2708(9)	0·739	0·92	$\dfrac{100}{99\,08}$	0·1472	[182·9 (183)] *184*
(6.) 0·1548	[0·2862(3)] 0·2878(9)	0·70	0·88	$\dfrac{100}{99\cdot12}$	0·1562	[183·2] *184·3*
(7.) 0·2039	[0·3783(4)] 0·3799(800)	0 62	0·785	$\dfrac{100}{99\cdot22}$	0·2055	[184·1] *184·9*
(7'.) 0·2039	[0·3784] 0·3800	0·665	0·83	$\dfrac{100}{99\cdot17}$	0·2056	[184·1] *184·9*

* Ice-cap on the bulb of the thermometer.

In the above tables under a and β two values are given. In the case of cane-sugar, alcohol, and urea (with the exception of the solution of urea which contains 0·001813 molecules per litre) there were, with all concentrations, fine needles of ice in the solution, but no ice-cap on the thermometer. In square brackets there are given under a and β the values which have been obtained when the freezing-point of water, as read off when there was a well-closed ice-cap round the bulb of the big (and the little) thermometer, is taken as the true zero ; the other figures (without brackets) under a and β are obtained when the freezing-point of water, as read off when there is no ice-cap round the bulb, is taken as the true zero.

In the latter case (of a well-closed ice-cap) the freezing-point of water has been found to be under my experimental conditions on an average 0°·0016 higher *, and may err, like all determinations in very dilute solutions, by about 1, 2, or less often 3 ten-thousandths of a degree. In the above tables the figures and results are given exactly as they were obtained from the observations. In these tables, in the cases of cane-sugar and urea, Van't Hoff's constant appears very clearly if the completely closed ice-cap be avoided in the determination of the freezing-point of water, and would appear still more clearly if one were to make the allowable correction of from 1 to 2 or 3 ten-thousandths of a degree : in short, so far as the degree of exactitude of the method itself allows, Van't Hoff's constant appears very clearly. In the cases of alcohol and cane-sugar the values of β fall in the more dilute solutions short of 1·87 by about $1\frac{1}{2}$ per cent.

The importance of the question on which we are engaged induces me to point out that Van't Hoff's constant can also be demonstrated most distinctly, independently of the freezing-point of water. Since cane-sugar, urea, and alcohol can only be very little dissociated, we can determine the several depressions and concentrations, starting from a given solution which does not cause the formation of an ice-cap round the bulb of the thermometer (instead of taking water as the starting-point), and state the results in relation to this ; by this means any error which attaches to the determination of the freezing-point of water is eliminated. Starting, then, from the most dilute solution, in which no ice-cap was observed, the following results are obtained :—

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* The convergence temperature was here above the freezing-point temperature.

TABLE III.

Cane-sugar.

	$a.$	a corr.	$\beta = \dfrac{a}{a\text{ corr.}} \times 100$
8-1.	0·1624(5) / −0·0100(1) / =0·1524	0·086790 / −0·006602 / =0·08019	190·1
7-1.	0·1330	0·07018	189·5
6-1.	0·1124(3)	0·05959	188·6
5-1.	0·0910	0·04867	187
4-1.	0·0692	0·03726	185·7
3-1.	0·0479	0·02532	189·2
2-1.	0·0244	0·01295	188·4

Urea.

	$a.$	a corr.	$\beta = \dfrac{a}{a\text{ corr.}} \times 100$
6-2.	0·2007	0·10285	191·5
5-2.	0·1339	0·06952	193·5
4-2.	0·0668	0·03473	192·3
3-2.	0·0269(70)	0·01450	186·2

(Corr. +0°·0003)

Alcohol, C_2H_5OH.

	$a.$	a corr.	$\beta = \dfrac{a}{a\text{ corr.}} \times 100$
7'-2.	0·3450	0·1860	185·5
7-2.	0·3449(50)	0·1860	185·4 (185·5)
6-2.	0·2530	0·1367	185
5-2.	0·2358(9)	0·1277	184·7 (184·8)
4-2.	0·1424(5)	0·07735	184·1 (184·2)
3-2.	0·0477(8)	0·02595	183·8 (184·2)

Thus, by this plan, the constant 1·87 or 1·88 appears very satisfactorily in the case of sugar and urea, and in the case of alcohol the constant is only about $1\frac{1}{2}$ per cent. too small. The general run of the values of β in the cases of cane-sugar, urea, and alcohol, shows that in the more concentrated solutions the values obtained for the molecular lowering of the freezing-point are greater than 1·87, and that it is only as the solutions become more dilute that the constant 1·87 becomes apparent. Now Van't Hoff's laws were only deduced for very dilute solutions, for " ideal " solutions.

This year I repeated the investigations of cane-sugar, alcohol, &c. under more favourable conditions, where no closed ice-cap but ice-bands or network of ice are formed round the Hg bulb of the $\frac{1}{1000}°$ thermometer, and the convergence temperature was under the freezing-point temperature. The difference in the capsules is conditioned by the differing of the ice-crystal, which is brought into the over-cold liquid to crystallize it. When the convergence temperature is under the freezing-temperature, the correct freezing-point of water, as well as of solutions, is directly obtained with the ice-cap. [A consideration of the processes which take place at the freezing-temperature, when the convergence temperature is above and under the freezing-temperature, is of great interest and will form the subject of a separate communication.] Thus I have shown by this third method, that Van't Hoff's constant holds good in dilute solutions. Table I′. gives the experimental data obtained with the $\frac{1}{1000}°$ and $\frac{1}{100}°$ thermometer for cane-sugar, alcohol, and from these data Table II′. is deduced. The Van't Hoff constant appears very clearly, and is in the most dilute solution only about $1\frac{1}{2}$ per cent. less than 1·87. Table III′. gives the molecular depressions, starting from the most dilute solutions, for cane-sugar &c.

TABLE III′.

	α corr.	1/1000° Thermometer.		1/100° Thermometer.	
		a.	*β.*	*a.*	*β.*
2–1.	0·003985	0·0073	*183·2*	0·0069 (59)	173·1 (148·1)
3–1.	0·011687	0·0221	*189·1*	0·0218	186·5
4–1.	0·018727	0·0346	*184·7*	0·0339	181
5–1.	0·028437	0·0521	*183·2*	0·0519	182·5 &c.

Cane-sugar. (1/1000° thermometer.)

α.	γ.	δ.	ε.	φ.	b.	e.	c'.	k.	
0	·4870(1)°	7	·4870–·4871°	10	......	−1·75°	13	millim. 752 (13·5)	With ice-cap.
,,	,,	,,	,,	,,	......	,,	,,	,,	Without ice-cap.
0·004114	·4793(2)	7	·4792–·4793	10	1·339	−1·87	12	751·5 (12)	,, ,,
0·008068	·4716(7)	8	·4716–·4718	11	0·980(1)	−1·92	11·5	750·5 (11)	,, ,,
0·015656	·4566(7)	9	·4567–·4567	10	1·082	−1·87	11·5	750·2 (13·5)	,, ,,
0·022632	·4442(1)	8	·4441–·4443	10	0·963	−1·9	12	750 (13·5)	,, ,,
0·032255	·4266(7)	8	·4266–·4267	10	0·887	−1·9	12·7	750	,, ,,

Alcohol. (1/1000° thermometer.)

α.	γ.	δ.	ε.	φ.	b.	e.	c'.	k.	
0	·4838(9)	5	·4838–·4839	8	......	−1·8	9·5	744·3 (9·3)	With ice-cap.
0	,,	,,	,,	,,	......	,,	,,	,,	Without ice-cap.
0·005463	·4733(4)	6	·4733–·4734	8	0·915	−1·8	9·5	743·1 (9·5)	,, ,,
0·01086	·4622	6	·4622–·4621	8	0·887	−2	9·5	742·1 (9·5)	,, ,,
0·02414	·4390	6	·4390–·4392	8	0·800	−1·9	9·5	741·8 (9·5)	,, ,,
0·03688	·4149	6	·4149–·4150	8	0·897	−1·9	9·5	740·8 (9·5)	,, ,,
0·06088	·3691(2)	6	·3691–·3692	8	0·861	−2·05	9·5	740·4 (9·5)	,, ,,
0·09472	·3042(3)	6	·3042–·3043	8	0·727	−1·9	9·5	740 (9·5)	,, ,,

Table II'.

Cane-sugar. (1/1000° thermometer.)

	$a.$	$a.$	$k_1-k_2.$	a corr.	$b.$	$c.$	$d.$	a corr.	$\beta=\dfrac{a\ \text{corr}}{a\ \text{corr.}}\times 100.$
1.	0·004114	0·00780	millim. −0·5	0·0077	1·339	1·674	$\frac{100}{98\cdot33}$	0·004183	184·1
2.	0·008068	0·0054	−1·5	0·0150	0·980 (1)	1·225	$\frac{100}{98\cdot775}$	0·008168	183·7
3.	0·015656	0·0304	−1·8	0·0298	1·082	1·353	$\frac{100}{98\cdot647}$	0·01587	187·8
4.	0·022632	0·0429	−2	0·0423	0·963	1·204	$\frac{100}{98\cdot796}$	0·02291	184·6
5.	0·032255	0·0604	−2	0·0598	0·887	1·101	$\frac{100}{98\cdot899}$	0·03262	183·5

Cane-sugar. (1/100° thermometer.)

	$a.$	$a.$	$k_1-k_2.$	a corr.	$b.$	$c.$	$d.$	a corr.	$\beta=\dfrac{a\ \text{corr}}{a\ \text{corr.}}\times 100.$
		0·008	−0·5	0·0079				0·004183	188·8
		0·015(4)	−1·5	0·0148 (0·0138)				0·008168	181·2 (169)
		0·030	−1·8	0·0298				0·01587	187·8
		0·042	−2	0·0418				0·02291	182·5
		0·060	−2	0·0598				0·03262	183·5

Alcohol. (1/1000° thermometer.)

a_1	a.	$k_1 - k_2$.	a corr.	b.	c.	d.	a corr.	$\beta = \dfrac{a \text{ corr.}}{a \text{ corr.}} \times 100.$
0·005463	0·0105	millim. −1·2	0·0102	0·915	1·144	$\frac{100}{98·56}$	0·005526	184·6
0·01086	0·0216 cor.−0·0003	−2·2	0·0209 cor. 0·0206	0·887	1·109	$\frac{100}{98·89}$	0·010985	190·2 cor. 187·5
0·02414	0·0449(50) cor.+0·0003	−2·5	0·0442 cor. 0·0445	0·800	1·00	$\frac{100}{99·00}$	0·02438	181·3 cor. 182·6
0·03688	0·0689(90)	−3·5	0·0681	0·897	1·121	$\frac{100}{98·88}$	0·0373	182·6
0·06088	0·1147	−3·9	0·1135	0·861	1·076	$\frac{100}{98·92}$	0·06153	184·5
0·09472	0·1796	−4·3	0·1783	0·727	0·9088	$\frac{100}{99·09}$	0·09557	186·5

Alcohol. (1/100° thermometer.)

a_1	a.	$k_1 - k_2$.	a corr.	b.	c.	d.	a corr.	$\beta = \dfrac{a \text{ corr.}}{a \text{ corr.}} \times 100.$
	0·0110	−1·2	0·0108				0·005526	195·2
	0·020	−2·2	0·0197				0·010985	179·3
	0·046	−2·5	0·0456				0·02438	187
	0·069(70)	−3·5	0·0685 / 0·0695				0·0373	183·6 / 186·3
	0·115(6)	−3·9	0·1144 / 0·1154				0·06153	186·7 / 187·5
	0·179	−4·3	0·1783				0·06153	186·6

In any case, what has still to be said is, that there are present subsidiary causes which might in part affect the equation and the constant 1·87 : such as dilution-heat put forward by Van't Hoff himself, by Nernst, and recently by Dieterici and by Evans ; or as the formation of higher molecules, which I believe to be present in greater or lesser number in all solutions.   But the influence of such causes could only be slight, and the only relations here quite certainly expressed are those given by Van't Hoff in the equation $t = \dfrac{0 \cdot 02 \cdot T^2}{w}$.   Besides this I regard it for various reasons as very probable that the absolute value of the scale of my thermometer is, between $0°\cdot4900$ and $0°\cdot3900$ or $0°3600$, 1–2 per cent. too small.   My further investigations will decide this question.   In every case Van't Hoff's thermo-dynamical equation has found excellent confirmation in dilute solutions, much better even than most generalizations established on the thermodynamical basis.

The results of Loomis (Wied. *Ann.* li.) obtained with the $\frac{1}{100}°$ thermometer, which show a continuous decrease of the values of β, may now be calculated, starting from the most dilute solutions ($\frac{1}{100}$ mol. normal) (Table IV.).

The observations of Loomis (made with a $\frac{1}{100}°$ thermometer) extend to $\frac{1}{100}$ molecule-normal.   The lowering of the freezing-point for a $\frac{1}{100}$ molecule-normal solution of a "non-conductor" is about $0°\cdot0187$; with such a fall of the freezing-point no formation of an ice-cap round the bulb of the thermometer is possible.   Here we have taken the $\frac{1}{100}$ molecule-normal solution as starting-point, and the result is that Loomis's investigations point indubitably to Van't Hoff's constant.   In the case of cane-sugar the figure obtained with almost all the more dilute solutions is 187; in the case of urea and alcohol we obtain constants which are too small by 2 or 3 per cent.   But the fact that these constants are almost the same at all concentrations shows most clearly that Mr. Loomis has not correctly determined the strength of his original solutions—a mistake which does not depend on the method itself.   The low values of the molecular lowering of the freezing-point obtained by Loomis, values which for a $\frac{1}{100}$ normal solution are already too small by 10 and more per cent., may be therefore here attributed in the first place to incorrect determination of the freezing-point of water.   But the not unimportant fluctuations in the value of b in the cases of alcohol and urea (after the elimination of the error which may depend on the freezing-point of water), which will be noticed in the above tables, shows this, that results obtained with a $\frac{1}{100}°$ thermometer, in spite of the exactitude which

TABLE IV.

	Cane-sugar.				Urea.				Alcohol, C_2H_5OH.		
$\beta=\dfrac{a}{a.}$	$a.$	a corr.	$\beta=\dfrac{a}{a\ \text{corr.}}\times100.$	$\beta=\dfrac{a}{a.}$	$a.$	a corr.	$\beta=\dfrac{a}{a\ \text{corr.}}\times100.$	$\beta=\dfrac{a}{a.}$	$a.$	a corr.	$\beta=\dfrac{a}{a\ \text{corr.}}\times100.$
$\dfrac{(2-1)a}{(2-1)a}$	(0·01840)	(0·01)	(184)	$\dfrac{(2-1)a}{(2-1)a}$	(0·03557)	(0·02)	(1·779)	$\dfrac{(2-1)a}{(2-1)a}$	0·01790	0·01	179
$\dfrac{(3-1)a}{(3-1)a}$	0·03750	0·02	187·5	$\dfrac{(3-1)a}{(3-1)a}$	0·07345	0·04	183·6	$\dfrac{(3-1)a}{(3-1)a}$	0·03586	0·02	179·3
$\dfrac{(4-1)a}{(4-1)a}$	0·05584	0·03	186·1	$\dfrac{(4-1)a}{(4-1)a}$	0·16513	0·09	183·5	$\dfrac{(4-1)a}{(4-1)a}$	0·05568	0·03	185·6
$\dfrac{(5-1)a}{(5-1)a}$	0·07505	0·04	187·6	$\dfrac{(5-1)a}{(5-1)a}$	0·34969	0·19	184	$\dfrac{(5-1)a}{(5-1)a}$	0·07216	0·04	180·4
$\dfrac{(6-1)a}{(6-1)a}$	0·09442	0·05	188·8					$\dfrac{(6-1)a}{(6-1)a}$	0·09072	0·05	181·4
$\dfrac{(7-1)a}{(7-1)a}$	0·11350	0·06	189·1					$\dfrac{(7-1)a}{(7-1)a}$	0·12804	0·07	182·9
$\dfrac{(8-1)a}{(8-1)a}$	0·17266	0·09	191·8					$\dfrac{(8-1)a}{(8-1)a}$	0·16533	0·09	183·7
$\dfrac{(9-1)a}{(9-1)a}$	0·27141	0·14	193·9					$\dfrac{(9-1)a}{(9-1)a}$	0·20199	0·11	183·6
$\dfrac{(10-1)a}{(10-1)a}$	0·37464	0·19	197·2					$\dfrac{(10-1)a}{(10-1)a}$	0·23926	0·13	184
								$\dfrac{(11-1)a}{(11-1)a}$	0·27549	0·15	183·6

K 2

distinguishes Loomis's method in a great many points, are affected with greater experimental errors than Mr. Loomis supposes to be possible. The results which I have obtained with my $\frac{1}{100}°$ thermometer by a method which by far surpasses Loomis's method in precision, are more or less of the same character (see Table II'.). At the same time with the observations recorded above and made with a $\frac{1}{1000}°$ thermometer on cane-sugar, urea, and alcohol, similar observations were made with a $\frac{1}{100}°$ thermometer. The results obtained are affected by experimental errors of from $0°\!\cdot\!001$–$0°\!\cdot\!002°$, and even occasionally greater; and that means that we cannot use the $\frac{1}{100}°$ thermometer for minute readings in very dilute solutions. For with the $\frac{1}{100}°$ thermometer we have to deal with experimental errors which cannot easily be removed or eliminated. In the first place it is not easy to avoid errors of from 1 to 2 thousandths degree in making the readings, even with the use of a microscope and a micrometer-scale, although with the method mentioned above we are able to observe the obtained freezing-point during the 10 to 15 minutes occupied making several readings ; the more must that be the case with other methods, where the obtained freezing-point can be observed only a short time. Now even in solutions which are only diluted to $\frac{1}{25}$ or $\frac{1}{50}$ molecule-normal, an experimental error of $0°\!\cdot\!002$ makes a difference of about 3 to 5 per cent. (in the case of non-conductors) in the lowering observed, and therefore also in the calculated molecular lowering of the freezing-point. The $\frac{1}{100}°$ thermometer can therefore in very dilute solutions only give us qualitative data.

II. *Proof of* Arrhenius's *Generalization.*

We proceed to the generalization of Arrhenius. Van't Hoff showed by four different methods, that a law analogous to that of Avogadro was valid for solutions of non-electrolytes like cane-sugar ; it then became of importance to account for exceptional cases in which the depression of freezing-point was abnormal, and in particular the cases of salts, acids, and bases in aqueous solution. The explanation was given when Arrhenius showed that by two independent quite different methods, the observation of lowering of freezing-point and of the electrical conductivity of a solution, the same value would be obtained for the factor i, which denotes the ratio of the pressure actually exerted by the substance to the pressure which the substance would exert if it consisted entirely of undissociated molecules.

Arrhenius made determinations on about 40 bodies in moderately dilute solutions of various concentrations and verified

the law more accurately. From the intimate connexion which exists between Van't Hoff's laws and the dissociation theory, it follows also that the generalization of Arrhenius may find a more exact experimental confirmation in dilute solutions. Therefore a more exact confirmation of the generalization of Arrhenius in very dilute solutions is not only important on account of the great light which the theory of dissociation has thrown upon the two provinces of chemistry and physics, but it is also important inasmuch as thereby the laws of Van't Hoff will find in every point their more exact confirmation.

We found above the normal value of the molecular lowering of the freezing-point in the cases of cane-sugar, urea, and alcohol—substances belonging to the class of bad conductors of electricity. In the following Tables are given the results obtained with sulphuric acid, potassium chloride, dichloracetic acid, trichloracetic acid, and orthonitrobenzoic acid. First come the experimental data. (The meanings of α, γ, δ, ϵ, ϕ, b, c, c', k, have already been given with Table I.)

TABLE V.

Trichloracetic Acid.								
a.	γ.	δ.	ϵ.	ϕ.	b.	c.	c'.	k.
								millim.
0 *	·4842	7	·4842	8	0·950	−2	20·3	758
0 †	·4858(9)	9	·4858–·4859	10	0·768	−1·8	20·6	758
0·005132 †	·4666(7)	7	·4666–·4667	10	0·70	−1·7	20	758
0·010182 ‡	·4487	5	·4487	10	0·978	−2	19·5	757·9
0·017636 ‡	·4232(1)	6	·4232–·4233	10	0·852	−1·9	19	758
0·029761 ‡	·3798(9)	9	·3797–·3799	12	0·987	−2	18	758
0·0414 ‡	·3397(8)	6	·3397–·3399	10	0·827	−2	18	758
0 *	·4841	5	·4840–·4841	10	0·748	−1·8	17·5	757
0 †	·4857	...	......	...	......	......	......	757
0·04443 ‡	·3304	5	·3304	10	0·67	−1·8	17·8	757

Dichloracetic Acid.								
0 *	·4852	...	......	...	0·82			
0 †	·4867	...	......	...	0·80			
0·002573 *	·4758	...	......	...	0·795			
0·005125 *	·4669(70)	...	......	..	0·785			
0·010230 ‡	·4515	...	......	...	0·766			
0·015294 ‡	·4366(5)	...	......	...	0·730			
0·02032 ‡	·4220(1)	...	......	...	0·615			
0 *	·4834(5)	...	......	...	0·685			
0·027551 ‡	·3933	...	......	...	0·680			

* Ice-cap round the bulb of thermometer.
† The ice-cap is avoided in a manner described in *Zeitschr. phys. Chemie* xv.
‡ No ice-cap on the Hg bulb of the thermometer.

Table V. (*continued*).

Orthonitrobenzoic Acid.

a.	*γ.*	*δ.*	*ε.*	*φ.*	*b.*	*c.*	*c′.*	*k.*
0 †	·4855	9	·4855–·4856	6	0·8	−1·8	21	762·7
0 †	·4855(6)	5	·4855–·4856	6	0·78	−1·8	22	762·7
0·006169 ‡	·4667	8	·4866–·4867	9	0·78	−1·8	22	762·2
0·008318 ‡	·4607	8	·4606–·4608	10	0·734	−1·8	22·5	762·2
0·01197 ‡	·4518(9)	8	·4517–·4519	10	0·766	−1·8	23	762
0·015037 ‡	·4447(6)	8	·4446–·4447	8	0·778	−1·8	23·5	761·2
0·017083 ‡	·4385(6)	10	·4385–·4387	8	0·72	−1·8	23	760·5
0·02046 ‡	·4308	10	·4306–·4310	7	0·81	−1·8	23	760·4

Sulphuric Acid, SO_4H_2.

a.	*γ.*	*δ.*	*ε.*	*φ.*	*b.*	*c.*	*c′.*	*k.*
0 †	·4841(2)	9	·4841–·4842	10	...	−2	18	752·3
0 *	·4824(5)	5	·4824–·4825	10	...	−2	18	752·3
0·0007611 †	·4809	6	·4808–·4810	10	...	−2	18	752·3
0·008329 ‡	·4455	5	·4455	10	...	−2	18	752·3
0·015875 ‡	·4139	7	·4139	9	...	−2	18	752·3
0 *	·4814	10	·4813–·4815	8	...	−2	17	749·2
0 †	·4829	5	·4829	8	...	−2	17	749·5
0 †	·4829(30)	7	·4829–·4830	7	...	−2	17	749·5
0·00456 †	·4609	4	·4606–·4609	10	...	−2	17	749·5
0·00456 †	·4609	11	·4608–·4609	10	...	−2	17	749·5
0 †	·4842(3)	8	·4842–·4843	8	...	−1·8 bis to −2	19	752·7
0·00456 †	·4620(19)	8	·4619–·4620	12	...	−1·9	19	752·9
0·00456 †	·4620(19)	6	·4619–·4620	8	...	−1·9	19	753·5
0·008329 ‡	·4457(6)	7	·4456–·4457	9	...	−2	19	754·7
0 †	·4849	5	·4849	8	...	−2	18	755·8
0 †	·4849(50)	11	·4849–·4850	10	...	−2	18	755·8
0·008367 †	·4466(7)	6	·4466–·4468	10	...	−1·8 bis to −2	18·5	755·6
0·008367 †	·4465(6)	8	·4465–·4466	10	...	−1·8	19	755·6
0·015912 ‡	·4148	9	·4147–·4150	10	...	−1·8	19	755·5
0·03092 ‡	·3539(40)	6	·3539–·3540	10	...	−1·8	19	755·3
0·03092 ‡	·3540(39)	10	·3539–·3540	10	...	−2	19	755·3
0 †	·4839(40)	9	·4830–·4830	10	...	−1·8	18·5	753·3
0·04567 ‡	·2951(2)	10	·2951–·2955	11	...	−2	18·7	753·3
0·06740 ‡	·2118(9)	8	·2116–·2121	8	...	−1·8	19	753·2
0·09569 ‡	·1038(9)	9	·1038–·1039	8	...	−1·9	20	753·2
0 †	6·147		(Small thermometer.)		...	−2	18	
0·1436 ‡	5·590	7	5·589–5·591	8	...	−2	18	
0·18645 ‡	5·429(30)	8	5·428–5·430	8	...	−2	18	

* Ice-cap round the bulb of thermometer.
† The ice-cap is avoided in a manner described in *Zeitschr. phys. Chemie*, xv.
‡ No ice-cap on the Hg bulb of the thermometer.

From these experimental data are deduced the following Tables (Tables VI. 1–3).

In these Tables are given under a_1' the degrees of dissociation as deduced from the freezing-point, when the value of Van't Hoff's constant is taken to be 1·87 ; a_2 gives the degrees of dissociation as determined by electric conductivity by a careful interpolation. The result is that the agreement between the values a_1' and a_2 is excellent. I think, therefore, that the latent heat of ice is more correctly estimated at 80 than at 79 cal. It appears that the degrees of dissociation deduced from the freezing-point under a_1' are somewhat smaller than those deduced from electric conductivity. Now the values of a, a_1', and a_2 have been determined at various temperatures (from about 0° and 18° or 25°), and in view of the investigations of Kohlrausch and Ostwald (on acetic acid, &c.), we have good ground for presuming that the degree of dissociation deduced from electric conductivity would be somewhat smaller for the same concentration at lower temperatures. I also think—being, till lately, singular in this opinion—that we may assume that in the solutions there are always present, in greater or lesser number, still higher undissociated and dissociated molecules which cause greater or lesser deviations from the strict agreement of the degrees of dissociation as deduced from the freezing-point and from electric conductivity. But the most probable reason is, that the absolute value of the graduated scale of the $\frac{1}{1000}$° thermometer is, between 0·49 and 0·36, 1–2 per cent. too small. From various causes I regard this as very probable. My further investigations will decide this question. In every case we ought, no doubt, in our calculations of the degrees of dissociation to use in all our given concentrations, or in concentrations measured by the scale 0·49 to 0·36, the value 1·84 or 1·85 instead of the theoretical 1·87, since we have practically found in the case of non-electrolytes under similar conditions in the more dilute solutions the value 1·85 or 1·84. If we do so, the law of Arrhenius finds in the observations given above the most wonderful, unexpected confirmation. See in the table above, a_1 and a_2. In any case, look at the above results how we may, there is no doubt that the law of Arrhenius has found remarkable confirmation in the cases of the non-conductors cane-sugar, urea, and alcohol, and of the conductors potassium chloride, sulphuric acid, dichloracetic acid, trichloracetic acid, orthonitrobenzoic acid.

TABLE VI. (1).

Sulphuric Acid, SO₄H₂. (1/1000° thermometer.)

a.	a.	b.	c.	d.	a corr.	$\beta = \dfrac{a}{a\ \text{corr.}} \times 100.$	$i = \dfrac{\beta}{1\cdot84}.$	$i' = \dfrac{\beta}{1\cdot87}.$	Generalization of Arrhenius.		
									a_1^* fr. p.	$a_1'^*$ fr. p.	$a_2\dagger$ elect. cond.
0·0007611	0·0032(1)	0·765	0·92	$\frac{100}{99\cdot08}$	0·0007687	429·3	.....	229·5	(In fluence of		NH₃.)
0·008329	0·0386(7)	0·775	0·93	$\frac{100}{99\cdot7}$	0·008404	459·3 (460·6)	249·6 (250·3)	245·6 (246·3)	74·8 ⎱ 75·2	72·8 (73·2)	77·2
0·015875	0·0702	0·785	0·94	$\frac{100}{99\cdot06}$	0·01603	437·9	238	234·2	69	67·1	72·7
,,	[0·0685]	,,	,,	,,	,,	[4273]					
0·00456	0·0220(1)	0·871	1·05	$\frac{100}{98\cdot95}$	0·004608	477·5 (479·6)	259·5 (260·65)	255·4 (256·5)	79·75 ⎱ 80·33	77·7 (78·25)	81·3
0·00456	0·0220(1) [0]	0·876	1·05	$\frac{100}{98\cdot95}$	0·004608	477·5 (479·6)	259·5 (260·65)	255·4 (256·5)	79·75 ⎱ 80·33	77·7 (78·25)	81·3
,,	[0·0205]	,,	,,	,,	,,	[444·9]					
0·00456	0·0223	0·806	0·97	$\frac{100}{99\cdot03}$	0·004604	484·4	263·3	259	81·65	79·5	81·3
0·00456	0·0223	0·826	0·99	$\frac{100}{99\cdot01}$	0·004604	484·4	263·3	259	81·65	79·5	81·3
0·008329	0·0386	0·879	1·06	$\frac{100}{98\cdot97}$	0·008417	458·6	249·2	245·3	74·6	72·65	77·2

0·008367	0·0384	0·808	0·97	100/99·03	0·00845	465	252·8	248·7	76·4	74·35	77·25
0·008367	0·0384	0·779	0·93	100/99·07	0·008449	465·2	253·2	249	76·6	74·5	77·25
0·015912	0·0701(2)	0·767	0·92	100/99·08	0·01606	436·5	237·2	233·4	68·6	66·7	72·7
0·03092	0·1310	0·717	0·86	100/99·14	0·03119	420	228·3	224·6	64·15	62·3	66·1
0·03092	0·1310	0·822	0·98	100/99·02	0·03122	419·6	228	224·4	64	62·2	66·1
0·04567	0·1888	0·738	0·89	100/99·11	0·04608	409·7	[222·7]	219·1	[61·35]	59·55	63·1
0·06740	0·2721	0·602(3)	0·72	100/99·38	0·0679	400·7	[217·8]	214·3	[58·91]	57·15	58·91
0·09569	0·3801	0·698	0·84	100/99·16	0·0965	393·9	[214·1]	210·6	[56·55]	55·3	56·55

(1/100° thermometer.)

0·1436	0·557	0·405	0·49	100/99·51	0·1443	386	206·4	53·2	53·34
0·18645	0·718(7)	0·659	0·79	100/99·21	0·1880	381·9	204·2	52·1	51·82
					(381·4)		(203·9)	(51·95)	

* $a_1 = \dfrac{i-1}{2}$, $a_1' - \dfrac{i'-1}{2}$.

† $\mu_\infty = 374 \left(10^8 \dfrac{k}{m}\right)$.

TABLE VI. (2).

Dichloracetic Acid.   (1/1000° thermometer.)

$a.$	$a.$	$b.$	$c.$	$d.$	a corr.	$\beta=\dfrac{a}{a\,\text{corr.}}\times100.$	$i=\dfrac{\beta}{1\cdot84}.$	$i'=\dfrac{\beta}{1\cdot87}.$	Generalization of Arrhenius.		
									$a_1{}^{*}$ fr. p.	$a_1'{}^{*}$ fr. p.	$a_2{}^{\dagger}$ elect. cond.
0·002573	0·009	0·795	0·99	$\frac{100}{99\cdot01}$	0·002599	361·7	196·6	193·4	96·6	93·4	95·6
0·005125	0·0182(3)	0·785	0·98	$\frac{100}{99\cdot02}$	0·005177	351·6 / 353·5	191·1 (192·1)	1·88 (1·89)	91·1 (92·1)	88 {89}	91·3
0·010230	[0·0337]	0·766	0·96	$\frac{100}{99\cdot04}$	0·01033	[326·2]					
„	0·0352	„	„	„	„	340·8	185·2	1·823	85·2	82·3	84·3
0·015294	[0·0486(7)]	0·730	0·91	$\frac{100}{99\cdot09}$	0·015447	[314·6 (315·2)]					
„	0·0501(3)	„	„	„	„	324·3 (325·6)	176·3 (177·0)	1·737 (1·747)	76·3 (77·0)	73·7 (74·1)	80·6
0·02032	[0·0632]	0·615	0·77	$\frac{100}{99\cdot23}$	0·02048	[308·6]					
„	0·0647(8)	„	„	„	„	315·9 (316·4)	171·7 (172)	1·692	71·7 (72)	69·2	73·1
0·027551	[0·0849]	0·680	0·82	$\frac{100}{99\cdot18}$	0·02778	[305·6]					
„	0·0864	„	„	„	„	311·0 (311·4)	169 (169·2)	1·663	69 (69·2)	66·3	70·3

Table VI. (2) *(continued).*

Orthonitrobenzoic Acid. (1/1000° thermometer.)

a.	a.	b.	c.	d.	a corr.	$\beta = \dfrac{a}{a\ corr.} \times 100.$	$i = \dfrac{\beta}{1\cdot 84}.$	$i' = \dfrac{\beta}{1\cdot 87}.$	Generalization of Arrhenius.		
									$a_1{}^*$ fr. p.	$a_1{}'{}^*$ fr. p.	$a_2\dagger$ elect. cond.
0·006169	0·0188(9)	0·780	0·94	$\frac{100}{99\cdot06}$	0·006227	301·9 (303·5)	164·1 (164·9)	1·614 (1·623)	64 (64·9)	61·4 (62·3)	62·8
0·008318	0·0248(9)	0·734	0·88	$\frac{100}{99\cdot12}$	0·008391	295·6 (296·8)	160·6	1·581 1·587	60·6	58·1 (58·7)	56·3
0·01197	0·0337	0·766	0·92	$\frac{100}{99\cdot08}$	0·01208	279	151·65	1·492	51·65	49·2	,,
0·015037	0·0408(9)	0·778	0·94	$\frac{100}{99\cdot06}$	0·01518	268·8 (269·4)	146·1 (146·4)	1·437 (1·441)	46·1 (46·4)	43·7 (44·1)	,,
0·017083	0·0470	0·721	0·87	$\frac{100}{99\cdot13}$	0·01723	272·6	148·1	1·458	48·1	45·8	
0·02046	0·0547(8)	0·812	0·97	$\frac{100}{99\cdot03}$	0·02066	264·7 (265·5)	143·85 144·3	1·415 (1·42)	43·85 44·3	41·5 (42)	,,

* In the case of orthonitrobenzoic acid, trichloracetic acid, dichloracetic acid, potassium chloride, $a_1 = i - 1$, $a_1' = i' - 1$.

† In the case of orthonitrobenzoic acid, trichloracetic acid, dichloracetic acid, measurements of W. Ostwald (25°), in the case of ClK measurements of Kohlrausch (18°). μ_∞ for ClK is $= 123$ (Kohlrausch).

Table VI. (2) (*continued*).

Trichloracetic Acid.   (1/1000° thermometer).

a.	a.	b.	c.	d.	a corr.	$\beta = \frac{a}{a\,\text{corr.}} \times 100$.	$i = \frac{\beta}{1\cdot84}$.	$i' = \frac{\beta}{1\cdot87}$.	a_1* fr. p.	$a_1'*$ fr. p.	$a_2\dagger$ elect. cond.
0·005132	[0·017516]	0·70	0·84	$\frac{100}{99\cdot16}$	0·005176	[340]					
,,	0·0191(2) corr.+0·0003	,,	,,	,,	,,	369 (371)	(200·5) corr. 198·8	1·973	(100·5) corr. 98·8	97·3	96·9
0·010182	[0·0355]	0·978	1·17	$\frac{100}{98\cdot83}$	0·0103	[344·7]					
,,	0·0371(2)	,,	,,	,,	,,	360·2 (361·2)	195·75 (196·3)	1·926 (1·932)	95·75 (96·3)	92·6 (93·2)	94·1
0·017636	[0·0611]	0·852	1·03	$\frac{100}{98\cdot97}$	0·01782	[342·8]					
,,	0·0627(8)	,,	,,	,,	,,	351·8 (352·4)	191·2 (191·5)	1·879 (1·884)	91·2 (91·5)	87·9 (88·4)	92·1
0·029761	[0·1043(4)]	0·987	1·18	$\frac{100}{98\cdot82}$	0·03012	[346·3]					
,,	0·1059(60)	,,	,,	,,	,,	352	191·3	1·882	91·3	88·2	90·2
0·0414	0·1444(5)	0·827	0·99	$\frac{100}{99\cdot01}$	0·04182	[345·3]					
,,	0·1461	,,	,,	,,	,,	349·4	[189·9]	1·868	[89·9]	86·8	,,
0·04443	0·1537	0·669	0·80	$\frac{100}{99\cdot2}$	0·04479	[343·2]					
,,	0·155300	,,	,,	,,	,,	346·5	[188·3]	1·853	[88·3]	85·3	,,

Potassium Chloride, ClK.. (1/1000° thermometer.)

a.	a.	b.	c.	d.	a corr.	$\beta = \dfrac{a}{a\ \text{corr.}} \times 100.$	$i = \dfrac{\beta}{1.84}.$	$i' = \dfrac{\beta}{1.87}.$	Generalization of Arrhenius.		
									$a_1{}^*$ fr. p.	$a_1'{}^*$ fr. p.	$a_2\dagger^*$ elect. cond.
0·009711	0·0352	0·87	1·08	100/98·92	0·009818	358·8	194·8	191·7	94·8	91·7	93·4
0·009711	0·0379	0·91	1·14	100/98·86	0·009822	358·3	194·7	190	94·7	90	
0·01934	[0·0677]	0·89	1·11	100/88·89	0·01956	[347·2]	192·55	189·5	92·55	89·5	91·6
,,	0·0693	,,	,,	,,	,,	354·3					
0·01934	[0·0676]	0·82	1·03	100/98·97	0·01954	[345·9]	192·4	189·4	92·4	89·4	
,,	0·0692	,,	,,	,,	,,	354·1					
0·03845	[0·1356]	0·811	1·01	100/98·99	0·03884	[349·5]	192·1	188·9	92·1	88·9	89·1
,,	0·1372	,,	,,	,,	,,	353·4					
0·03845	[0·1349]	0·792	0·99	100/99·01	0·03883	[347·6]	191·1	188	91·1	88	
,,	0·1365	,,	,,	,,	,,	351·7					
0·07606	[0·2655]	0·481	0·60	100/99·4	0·07652	[347·0]	[189·8]	186·7	[89·8]	86·7	87·5
,,	0·2671	,,	,,	,,	,,	349·2					
0·07606	[0·2658]	0·651	0·81	100/99·19	0·07668	[346·7]	[189·7]	186·5	[89·7]	86·5	
,,	0·2674	,,	,,	,,	,,	348·8					

* For footnote, see above.

† For footnote, see above.

III. *The Law of Dilution as deduced from the Freezing-Point.*

We proceed to illustrate one of the most important, if not the most important, of the foundations of the theory of dissociation, namely, Ostwald's law of dilution based upon the freezing-point. (Planck's name also should be mentioned here.) It was notably Ostwald who first showed the relation between the numbers of dissociated and undissociated molecules to depend upon the action of mass, and who took the pains to verify the same experimentally in the case of two hundred acids by means of their electric conductivity. From the above-mentioned generalization of Arrhenius it follows that the law of dilution ought also to be deducible from the freezing-point, since the freezing-point as well as the electric conductivity enables one to know the degree of dissociation, and it may be at the same time interesting, inasmuch as we have not here to do with velocity of ions or with the theory of the electric conductivity. On the other hand, from the intimate connexion which exists between Van't Hoff's laws and the dissociation theory, it follows that the law of dilution must find its experimental confirmation in dilute solutions. This has not been possible before now, because the constant deduced from the law of dilution is greatly affected by the experimental error, and the freezing methods were till now far from being sufficiently exact for this purpose. But we have now made a sufficient advance in the freezing methods to be able to undertake this proof under favourable circumstances. Here we have to take into account two conditions : first, the degree of dissociation must not be small, especially because, in consequence of the nature of the calculation, the experimental error affects not the whole value observed, but only that part of it which gives the degree of dissociation; secondly, the degree of dissociation must very considerably change with the degree of dilution, or else the influence of dilution is difficult to ascertain. The law of dilution can therefore only be proved in the case of a few substances which fulfil these conditions. Dichloracetic acid and orthonitrobenzoic acid are suitable for this purpose.

Below are given the constants calculated according to the law of dilution in the cases of dichloracetic acid and orthonitrobenzoic acid. In the last Table are given under " *a* corrected " the concentrations of the solutions, and under Δ the degree of dissociation, when $t = 1\cdot87$. The constant K given by the law of dilution appears indubitably, but is smaller

Dichloracetic Acid. (1/1000° therm.)

α corr.	Δ'.	Δ'².	1−Δ.	$\frac{\Delta'^2 \cdot a}{1-\Delta} = K'$. The law of Dilution.	Δ.	Δ².	1−Δ.	$\frac{\Delta^2 \cdot a}{1-\Delta} = K$. The law of Dilution.
0·005177	91·1 (92·1)	8300 (8410)	8·9 (7·9)	4·828 (5·516)	88 (89)	7743 (7920)	12 (11)	3·341 (3·727)
0·01033	85·2	7259	14·8	5·066	82·3	6773	17·7	3·952
0·015447	76·3 (77)	5822 (5929)	23·7 (23)	3·794 (3·989)	73·7 (74·1)	75439 (5498)	26·25 (25·85)	3·199 (3·284)
0·02048	71·7 (72)	5141 (5183)	28·3 (28)	3·791 (3·792)	69·2	4789	30·8	3·184
0·02778	69 (69·2)	4761 (4788)	31 (30·8)	4·266 (4·319)	66·3	4396	33·7	3·623

Orthonitrobenzoic Acid. (1/1000° therm.)

α corr.	Δ'.	Δ'².	1−Δ.	$\frac{\Delta'^2 \cdot a}{1-\Delta} = K'$. The law of Dilution.	Δ.	Δ².	1−Δ.	$\frac{\Delta^2 \cdot a}{1-\Delta} = K$. The law of Dilution.
0·006227	64·1 (64·9)	4109 (4212)	35·9 (35·1)	·7123 (·7471)	61·4 (62·3)	3774 (3882)	38·57 (37·7)	·6093 (·6411)
0·008391	60·6	3672	39·4	·7821	58·1 (58·7)	3376 (3446)	41·9 (41·3)	·676 (·700)
0·01208	51·65	2668	48·35	·6669	49·2	2421	50·8	·5757
(0·01518)	[46·1 (46·4)]	[2125 (2153)]	[53·9 (53·6)]	·5985 (·6098)	[43·7 (44·1)]	(1945)	(55·9)	(·5281)
0·01723	48·1	2314	51·9	·7687	45·8	2098	54·2	·6664
0·02066	43·85 (44·3)	192·3 (196·2)	56·15 (55·7)	·7075 (·7288)	41·5 (42)	172·3 (176·4)	58·5 (58)	·6083 (·6283)

Trichloracetic Acid. (1/1000° therm.)

α corr.	Δ'.	Δ'².	1−Δ.	$\frac{\Delta'^2 \cdot a}{1-\Delta} = K'$. The law of Dilution.	Δ.	Δ².	1−Δ.	$\frac{\Delta^2 \cdot a}{1-\Delta} = K$. The law of Dilution.
0·0103	95·75 (96·3)	9168 (9273)	4·25 (3·7)	25·81 (22·22)				
(0·01782)	[91·2 (91·5)]	[8318 (8371)]	[8·8 (8·5)]	[16·85 (17·55)]				
0·03012	91·3	8335	8·7	28·75				
0·04182	89·9	8081	10·1	33·45				
0·04479	88·3	7796	11·7	29·84				

than that deduced from electric conductivity (25° Ostwald). Much better is the agreement between the constant from freezing-point and the constant from electric conductivity, if the practically found $t = 1 \cdot 84$ is used ; the constant is well obtained then also in the case of trichloracetic acid. See Δ' and K' in Table VII.

I may be permitted to express my heartiest thanks to the authorities of Christ Church and to Mr. A. G. Vernon Harcourt for kindly placing the resources of their laboratory at my disposal.

Christ Church, Oxford.

VII. *Notices respecting New Books.*

Annals of British Geology, 1893. By J. F. BLAKE, *M.A.*, *F.G.S.* 8vo., xxiv and 365 pages, with 90 illustrations, February 1895. Dulau & Co., London.

THIS digest of Books and Papers published during the year (1893), with an Introductory Review, is a welcome continuation of three former volumes, already noticed in the 'Philosophical Magazine.' The subjects taken in order from page 1 to page 301 are :— 1. General Geology ; 2. Stratigraphical Geology ; 3. Palæontology ; 4. Palæobotany ; 5. Mineralogy ; 6. Petrology ; 7. Economical products ; 8. Maps and Sections relating to England and Scotland. Notices of notes and memoirs on Foreign Geology, published in Britain, taken in much the same order as the above, occupy pages 302–353. Three good Indexes are found at pages 355–365.

The aim of this work is to provide annually for students of Geology a condensed account of all that has been done in the science so far as the British Islands are concerned. For this purpose the various papers and other publications are classified under larger and smaller subdivisions, so that the whole work is a kind of subject-index.

The several papers are either merely recorded, or more or less fully abstracted. The "Introductory Review" aims at giving a succinct account of the general progress in Geological Science, and treatment of disputed questions, during the year concerned, based on the information afforded by the said publications. Where desirable and convenient, especially with new species of fossils, figures (copied by "process") are given in the text. In the abstracts of the papers the ideas advanced or supported by the several authors are represented from their own points of view ; in the "Introductory Review" the reviewer (he objects to be regarded as a "compiler" of this most careful and laborious work) writes critically on his own responsibility.

The number of publications dealt with each year has varied

between 550 and 740, and the accounts of them, varying in length from 17 pages downwards, have for the most part been revised by the respective authors. While serving as a guide to the original papers, the "Annals" is primarily intended for those who cannot see the originals at all, and is therefore planned so as to contain in itself in the course of a few years the whole body of recent Geological knowledge in this country.

We are glad to find that there is an increasing public support of this useful work; and that, if the present volume proves to be self-supporting, we may look hopefully to its future.

The Morphology of Crystals. By Professor N. STORY MASKELYNE, *F.R.S.* (Clarendon Press. 1895.)

THE appearance of Prof. Maskelyne's long-expected book is an event of considerable importance in the mineralogical world. The lines on which the book is written were fixed some twenty years or more ago, and a good deal of it has been long in print. One cannot help regretting that Prof. Maskelyne had not the courage to publish the book in parts. The first 150 pages or more are, we fancy, much in the same state that they were twenty years ago. They contain the general propositions which hold for all crystals, and amongst others the elegant proof of the theorem, that the only angles possible between planes of symmetry in a crystal are one or other of the four following—60°, 90°, 120°, and 180°. This proof Prof. Maskelyne used to give more than twenty-five years ago in his lectures at Oxford, but it has remained inaccessible to the generality of students.

Prof. Maskelyne may, in his manner of regarding the subject, be almost classed as a member of the Vienna school of Grailich and von Lang. He adopts, as they did, planes of symmetry as the all important elements in classification, and axes of symmetry receive but a small amount of attention. In the last decade there has been a very decided movement in the direction of regarding crystal forms as resulting from the general principles of symmetry, and more especially to base the subdivision into types on the nature and number of the axes of symmetry. This latter method is certainly more logical, and has rendered it needless to talk of planes, or axes, of symmetry being in abeyance. A crystal has certain elements of symmetry which have, if many coexist, definite relations existing between them, and which in themselves form a complete cycle. The application of the methods of analytical geometry to the representation of crystal faces may, however, owing to the law of rational indices, indicate the possibility of faces which have a higher geometric symmetry than that of the crystal. We may illustrate this by a truncated cone of cannon-balls. If the balls be spheres, the base and planes of truncation will clearly be exactly similar parallel faces. If the shot be modern cylindrical ones pointed at one end, and if these be placed in the pile with the base downwards, the base and plane of truncation will be parallel but

no longer similar physically. The base will have all the circular bases of the shot in it; the upper plane only the apices. The two types are distinct structures, and the connexion between the parallel faces is only a geometric one. In Prof. Maskelyue's book the cylindrical pile would be regarded as a hemihedral form of that of round shot arising from a loss of the centre of symmetry. With this change of view goes, of course, a somewhat radical change in the technical terms used to denote the type to which the crystal belongs. The technical words used in the book are somewhat complicated, and not always easy to comprehend and remember. They are also rather numerous, and it is questionable whether many of them will live. The phraseology in the new view has, as far as the English student is concerned, yet to be created.

The early portion, to which we have already alluded, is taken up with the general relations which exist between the faces possible on a crystal, subject, that is, to the law of rational indices. The mathematical treatment is elegant, though in some cases it is capable of considerable simplification; as is the case, for instance, in M. Cèsaro's beautiful proof of the rationality of the anharmonic ratio of four tautozonal planes. Prof. Maskelyne's treatment is a great advance on anything which has emanated from the active pens of our German friends. Of course a good deal of it follows closely that of the late Prof. Miller, as, *e. g.*, the elegant way of obtaining formulæ for the transformation of the axes of reference. But Prof. Maskelyne has not been so anxious as his predecessor to abbreviate his discussion, and his proofs are therefore more easily followed and less artificial.

A marked and excellent feature of the book is the amount of space given to the discussion of those remarkable crystalline aggregates known as twins. A good deal of the preparation for the matter in this portion is probably due to Prof. Maskelyne's friends at the Natural History Museum. The discussion of the more conspicuous instances in each system is fairly complete. The fictitious nature of the twin-axis is carefully pointed out, but one regrets that the confusing term "twin-plane" has been retained. As a term for a plane perpendicular to the axis it is not wanted, and I fear its use in this sense is too well established for it to be employed in a more rational way. All mineralogists will appreciate the excellence of the treatment of the troublesome and confused twins of the anorthic felspars. The views of the many distinguished crystallographers who have written on them are clearly stated and most carefully illustrated by well-drawn diagrams. The error made in one instance by the late Prof. vom Rath in the calculation of the so-called rhombic section is detected. Attention has already been called to it many years ago, but like other errors it has great vitality, as is shown by its remaining uncorrected in that monument of learning and conscientious work, Mr. E. S. Dana's recent edition of his father's 'Mineralogy.' Doubts are justly thrown on this rhombic section, but research

will alone decide whether it is to hold the place in the theory of these twins which vom Rath assigns to it.

The book is an inestimable boon to the student, who will find in it a store of information. Unfortunately one trifling matter—a legacy from Prof. Miller—will much interfere with its success as a text-book, and will, we fear, at no distant future necessitate a new edition and modification of many of the beautiful diagrams of crystal forms with which it is bountifully supplied. This misfortune arises from the orientation of the axes of X and Y. All Continental and American writers have long adopted one in which Miller's orientation is inverted. And the amount of literature in which this inverted arrangement is used is now so great that it is hopeless to expect ever to change it. It is a trifle in itself, but anyone familiar with the liability to error in changing a notation, and the confusion which a slight error in notation introduces, will recognize its force. To a student, however, who is not troubling himself with the literature of minerals, it will cause little inconvenience in the use of the book.

It would be difficult to praise too highly the printing, and more especially the illustrations, of the book. A better illustrated book on crystallography has, we think, never been published.

VIII. *Proceedings of Learned Societies.*

GEOLOGICAL SOCIETY.

[Continued from vol. xxxix. p. 547.]

January 9th, 1895.—Dr. Henry Woodward, F.R.S., President, in the Chair.

THE following communications were read :—

1. 'The Formation of Oolite.' By E. B. Wethered, Esq., F.G.S.

2. 'On the Lias Ironstone aronnd Banbury.' By Edwin A. Walford, Esq., F.G.S.

The ferruginous limestone of the Middle Lias of the Banbury district occurs practically within a ten-mile circle around Banbury. The stone (the Marlstone of the Geological Survey) is an 'oolitic' cyprid-limestone with much molluscan and crinoidal débris and some quartz-grains. The author describes the lithological characters of the rock, and their variations, as traced laterally and vertically, giving a full description of its local development, with a detailed account of the sections in the principal exposures. The marlstone of this area is dissimilar from that of Gloucestershire both in appearance and in fossil contents, the Gloucestershire stone being of earlier deposition and representing better the base of the Banbury series, rather than the stratum which is richest in iron. From the blue clays of the *Margaritatus*-zone up to the rock-bed itself there is a slow change of conditions, and the fauna points to tranquil

sublittoral conditions. The author reserves his views as to how the rock-bed obtained its ferruginous elements.

He gives a description of the palæontology and economic uses of the deposits, and appends analyses of various ironstones from the district, made by the aid of Sir B. Samuelson.

3. 'Notes on the Geology and Mineral Resources of Anatolia (Asia Minor).' By W. F. Wilkinson, Esq., F.G.S.

The route traversed from northwards to southwards through the city of Broussa lay through a country composed of sedimentary rocks (largely limestones with some shales and conglomerates). In the mountains metamorphic rocks were met with, and also igneous rocks. The principal igneous rocks noticed are granites and serpentines; in the latter chrome-iron-ore occurs, and is worked.

January 23rd.—Dr. Henry Woodward, F.R.S., President, in the Chair.

The following communications were read :—

1. 'Carrock Fell: a Study in the Variation of Igneous Rock-masses. Part II. The Carrock Fell Granophyre. Part III. The Grainsgill Greisen.' By Alfred Harker, Esq., M.A., F.G.S.

The augite-granophyre of Carrock Fell is first described in its normal development, special attention being drawn to the various types of micrographic intergrowths which it exhibits. The variation of the rock is next examined, and, in particular, a curious basic modification which occurs near its junction with the gabbro described in a former paper. The granophyre here passes into a coarse type rich in augite, iron-ores, and apatite, its silica-percentage falling to as low as 58. The author attributes this to the acid magma having incorporated in itself portions of the highly basic margin of the gabbro. The latter rock seems to have been fused or dissolved by the magma, with the exception of certain of its more refractory minerals which survive in the modified marginal part of the granophyre.

The latter part of the paper deals with a remarkable quartz-mica-rock found on the north side of the Skiddaw granite. It differs in some respects from the Cornish greisens, and resembles in its mode of occurrence certain pegmatites in the Scottish Highlands. The author considers the rock to have been extruded from the granite in connexion with the post-Silurian crust-movements of the district, while its composition has probably been further modified by subsequent chemical changes.

2. 'The Geology of the Country around Fishguard (Pembroke-shire).' By F. R. Cowper Reed, Esq., B.A., F.G.S.

The tract of country forming the subject of this communication occupies the northern part of Pembrokeshire, from Newport to Strumble Head. All the beds are of Ordovician age, with the possible

exception of those on Dinas Island, and have a general east-to-west strike with a high dip to the north. Arenig Slates occupy the southern part of the district. Typical Llanvirn Beds with the *Placoparia*-fauna occur at Fishguard, and above them the *Didymo-graptus Murchisoni*-zone of the Lower Llandeilo is found. On this horizon are the first traces of volcanic activity : acid lavas and tuffs are here interbedded with the slates. The Middle Llandeilo is partly faulted out in Goodwick Bay, and near Newport is penetrated by huge intrusive sheets of diabase. The Upper Llandeilo is marked near its base by a thick zone of lava-flows, which are overlain by fossiliferous shales. Hartfell graptolites have been found in the overlying grey and black slates. The lavas and breccias on Strumble Head are held to be on the same horizon as those near Newport.

All the lavas are acid ; some are soda-potash felsites. Nodular, banded, and perlitic structures are sometimes visible. Crypto-crystalline, microlitic, and micropoikilitic types of groundmass are possessed by these lavas ; the latter type is held to be probably a contact-phenomenon. The intrusive masses consist of diabase, with important tachylytic and variolitic modifications.

3. 'On the Mean Radial Variation of the Globe.' By J. Logan Lobley, Esq., F.G.S.

The author submits considerations (chiefly derived from the characters of the earlier sediments) which lead him to suppose that crust-folds have not been produced by continuous contraction of the Earth, and that the planetary heat and mean radius of the Earth have been practically invarible during the period which has elapsed since Cambrian times.

February 6th.—Dr. Henry Woodward, F.R.S., President,
in the Chair.

The following communications were read :—

1. 'On Bones of a Sauropodous Dinosaur from Madagascar.' By R. Lydekker, Esq., B.A., F.R.S., V.P.G.S.

2. 'On the Physical Conditions of the Mediterranean Basin which have resulted in a Community of some Species of Freshwater Fishes in the Nile and the Jordan Waters.' By Prof. E. Hull, M.A., LL.D., F.R.S., F.G.S.

The author summarizes the evidence in favour of the existence of barriers in post-Miocene times, separating the Mediterranean area into a chain of basins. He brings forward arguments in support of his contention that the waters of the eastern (Levantine) basin became fresh during a period when the area of evaporation was smaller, and the supply of river-water greater, than at present. Into this freshwater lake the waters of the Nile would flow directly. He has elsewhere given reasons for believing that the Jordan Valley from Lake Huleh to Arabah was the bed of a lake over 200 miles

long, and at least 1300 feet above the present level of the Dead Sea. He suggests that the waters of this lake escaped into the Levantine basin through the plain of Esdraelon. With such physical conditions existing, the fauna of the Levantine basin would have a means of spreading throughout the whole system of waterways connected with it.

In conclusion the author adds some observations on the changes which occurred in the Mediterranean area subsequent to the post-Miocene epoch of earth-movement.

3. 'On the Loess and other Superficial Deposits of Shantung (Northern China).' By S. B. J. Skertchly, Esq., and T. W. Kingsmill, Esq., C.E.

The following deposits are described in the order of their antiquity :—

1. Recent Fluviatile deposits.

2. Marine sands with *Cardium*, *Ostræa*, and *Bulla*, extending to a height of 200 feet above sea-level, and indicating former submergence to that amount.

3. Old River-gravels, often resting on loess, and possibly contemporaneous with the marine gravels. They furnish part of the evidence relied on by the authors for supposing the existence at that time of a climate moister than the present one.

4. Loess.

5. Basement-gravels having the same relation to the loess that the Upper Greensand bears to the Chalk.

The loess east of the Pamirs is extensively developed over an area of over one million square miles. It is sometimes over 2000 feet thick, and occurs up to several thousand feet above sea-level.

Evidence is brought forward by the authors with the intention of establishing the absolute want of connexion between the Chinese loess and the present river-systems, its original stratified condition (as shown by variation of tint and horizontality of layers of concretions), and its subsequent rearrangement to a great extent. The absence of marine shells is discussed, and the suggestion thrown out, with diffidence, that the shells have been destroyed by percolating water.

The authors give their reasons for supposing that the loess is a marine formation, and state that the sea need not have reached to a higher level than 600 feet above the present sea-level, for the Pamir region where it occurs, 7000 feet above the sea, is an area of special uplift.

They maintain that there are no proofs of the glaciation of Northern and Eastern Asia, so that the Chinese loess can have no connexion with an area of glaciation. They state that the zoological, ethnological, historical, and traditionary evidence alike point to the former depression of Asia beneath the sea, and the subsequent desiccation of the land, consequent upon re-elevation.

February 20th.—Dr. Henry Woodward, F.R.S., President,
in the Chair.

The following communications were read :—

1. 'Contributions to the Palæontology and Physical Geology of the West Indies.' By J. W. Gregory, D.Sc., F.G.S.

The earlier part of the paper is largely concerned with the corals of the raised reefs of Barbados, and, on account of the confusion in the synonymy of the West Indian corals, the synonymy of the species is given in some detail. A list of the mollusca of the Low-level reefs follows.

The occurrence of the 'Oceanic Series' of beds over wider areas than generally recognized is proved by the existence of Radiolarian Marls in Cuba, as announced in the discussion on Messrs. Jukes-Browne and Harrison's paper (Q. J. G. S. vol. xlviii. 1892). The author gives a list of species of Radiolaria from the Cuban deposit, all of which are also found in that of Barbados. Additions to the fossil fauna of Antigua are recorded.

In discussing the age of the Barbados rocks, the author states that there is now no doubt that the following is the sequence (in descending order) :—

Raised Coral Reefs. { Low Level : Pleistocene.
{ High Level : Pliocene.
Oceanic Series ...... { *Archæopneustes-abruptus-* { Miocene (and possibly partly
{ limestone. { Pliocene) and partly Oli-
{ Thalassic Marls. { gocene.
Scotland Beds ....Oligocene (probably Lower).

The fauna of the Low-level Reefs proves their late Pleistocene age. Until more mollusca are collected from the High-level Reefs, it will not be possible to decide whether the whole are Pleistocene, or whether some must be included in the Pliocene ; it is probable that the latter will have to be done. The Scotland Beds are referred to the Oligocene. This narrows the limit for the time of formation of the deep-sea oozes. Further light is thrown on this question by examining the evidence for the period of submergence of the Panama Isthmus, from consideration of the resemblances of the marine faunas on either side, and the earliest migrations of terrestrial animals across the Isthmus since its elevation. The author puts the period of final emergence of the peninsula in Miocene, or possibly late Oligocene, times, and maintains that there is no evidence of the connexion of Atlantic and Pacific in this region since then.

He gives reasons for supposing that a subsidence of the Caribbean Sea was simultaneous with this emergence of the Isthmus, and that this subsidence plunged part of the area now occupied by land into abysmal depths in which were deposited the deep-sea oozes of Barbados, Trinidad, and Cuba. In some part of the Miocene or Pliocene re-elevation began, and shallower-water deposits (the *Archæopneustes*-limestone) were laid down. Elevation continued,

resulting in the formation of coral-reefs and their final uplift to different levels above the sea.

2. 'The Whitehaven Sandstone Series.' By J. D. Kendall, Esq., F.G.S.

The Whitehaven Sandstone, with its associated shales, is a purple-grey deposit sometimes having a thickness of 500 or 600 feet. The author gives details of a large number of sections of the series, which also contains thin coal-seams and occasionally *Spirorbis*-limestone.

He combats the view that it is stained Middle Coal-measure deposit, and gives his reasons for believing that it rests unconformably upon the Middle Coal-measures, and also that it has not received its colour by abstraction of colouring-matter from the Permian beds, but that the colour actually belongs to the deposit. He describes sections which lead him to suppose that the deposit has a wider distribution over the Cumbrian district than is allowed by previous writers.

3. 'Notes on the Genus *Murchisonia* and its Allies, with a Revision of the British Carboniferous Species, and Descriptions of some New Forms.' By Miss J. Donald.

IX. *Intelligence and Miscellaneous Articles.*

ON THE DOUBLE REFRACTION OF ELECTRICAL RAYS.
BY K. MACH.

THE experiments show that plates of wood cut parallel to the fibres behave towards electrical rays in just the same manner as plates of crystal cut parallel to the optical axis do towards the rays of light. The inquiry naturally suggests itself whether plates of wood which are cut at right angles to the fibres are singly reflecting in the direction of the latter, as the optical analogy suggests. The forestry collection of the Hohenheim Agricultural Academy provided me with materials for experiments in this direction : experiment confirmed the accuracy of the supposition. A plate of Scotch fir (*Pinus sylvestris*) almost a metre in diameter and 16 centim. in thickness, cut at right angles to the axis of the tree, being placed between the crossed mirrors, the path of the sparks remained dark even when the adjustment was most sensitive. The same result was obtained when a smaller plate of the same material, 70 centim. in diameter and 14 centim. thick, was introduced into the path of the rays, and even when both plates were joined so as to form one 30 centim. in thickness. A third plate of a dense and heavy kind of wood (*Sophora japonica*) was investigated, and in this case also the path remained dark.—Wiedemann's *Annalen*, No. 2, 1895.

X. *On the Use of the Globe in the Study of Crystallography.* By J. Y. BUCHANAN, *F.R.S.*[*]

THE use of the globe in Crystallography is twofold. It enables us to study the character and follow the details of the form of the solid projected radially on its surface. Also all the measurements which can be made on the solid itself can be as conveniently made on its projection on the sphere, and all calculations and developments connected therewith can be made by simple graphical construction and measurements on the sphere. The black globe, with the divided circles belonging to it, is a calculating machine adapted to the solution of all the problems to which the analytical methods of spherical trigonometry are usually applied.

To the student of crystallography, of astronomy, of mathematical geometry, and of geometry of three dimensions generally, the globe and its circles fill the same place as the drawing-board and scale do to the engineer and surveyor. A globe which is to be used for geometrical constructions should be quite free and unencumbered with the fixed axis usually met with in those intended for geographical or astronomical instruction. Also the divided circles with which measurements are made should be capable of being applied directly to the surface of the globe, so as to avoid errors of parallax. The globe which I have found most suitable for the purpose,

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[*] Read before the Chemical Society, December 6, 1894. Communicated by the Author.

and I have used it for a number of years, is one published by Mr. E. Bertaux, of 25 Rue Serpente, Paris. It has a diameter of 22 centimetres, and is covered either with black slate cloth for drawing on with slate pencil or chalk, or with parchment paper for drawing on with lead pencil. To this is adapted a system of divided circles of the same radius as the sphere, called the *métrosphère,* which is the invention of Captain Aved de Magnac, of the French navy. The métrosphère consists of one complete circular band of brass, the upper edge of which is a great circle of the sphere. It is divided into degrees throughout one half of its length, numbered from 0° to 180°. At right angles to this circle a semicircular band of the same radius passes across from one side to the other. The edge of this semicircle, which is turned towards the graduated half of the complete circle, springs from 0° and 180° respectively, and it coincides with a great circle of the globe. The combination of circle or equator and semicircle or meridian bridging its diameter resembles a crown. At the apex of the crown or pole of the equator a movable quadrant is pivoted. It can traverse the whole of the part of the sphere enclosed by the divided part of the equator and by the meridian, and it can be clamped anywhere in the divided part of the equator. The quadrant is divided into degrees, as is also the meridian. When in use the metrosphere rests on the globe, so that there is complete contact, and it can be shifted all over its surface. It is possible by its means to draw and measure any arcs or angles on the surface of the globe, and consequently to solve graphically all problems of spherical geometry with an accuracy which depends only on the dimensions and workmanship of the globe and metrosphere. It is convenient to have a scale of chords of arcs of great circles of the sphere, so that arcs may be measured or laid off with a pair of compasses. The real usefulness of the globe is not to be learned by theory or precept, but by actual experience in the solution of problems, whether the study be astronomy, or navigation, or geography, or crystallography. Within the bounds of a paper like the present it is possible only to show the general direction in which it is of use in the study of the last-named science.

The fundamental data for the determination of a crystal are the angles which its faces make with each other. These are measured with the goniometer. Let us follow the process as applied to a polyhedron of any number of plane faces, arranged in any way so as to completely enclose the space. The polyhedron or crystal is attached to the goniometer, by

means of which we can measure directly the angle included between the normals to any two faces : alongside, we have our globe with its metrosphere, on which we propose to enter the results obtained with the goniometer. We imagine the polyhedron situated inside the globe and concentrically with it ; then the normals to its faces are radii of the sphere, the surface of which they meet in points, which are called the poles of the faces. The angle included between any two such radii is measured by the great circle arc between the two corresponding poles, and it is equal to the angle between the two faces as given by the goniometer. Hence the angles between the faces as measured on the goniometer can be transferred directly to the globe, on which they are laid down as arcs.

We begin with the globe clean. Any point on it is chosen as the pole of the first face. From this point a great circle is drawn in any direction. When the angle between the first and the second faces has been measured, it is laid down on the globe as an arc of the same number of degrees of the great circle just drawn from the starting-point. The poles of the two faces, Nos. 1 and 2, are in the extremities of this arc, which is the *base line* of the survey of the crystal ; and, by triangulation from it, the poles of all the other faces can be laid down so soon as the angles between them have been measured on the goniometer or otherwise determined.

Consider a third face, No. 3, adjacent to Nos. 1 and 2, but not parallel to either of them. Let angles be measured between it and Nos. 1 and 2, and let these angles be transferred to the sphere as arcs. From pole No. 1, as centre, with the arc corresponding to the angles between Nos. 1 and 3 as radius, describe a circle on the sphere : similarly, with No. 2 as centre, and arc equal to the angle between Nos. 2 and 3 as radius, describe another circle. These circles cut each other in two points similarly situated on opposite sides of the arc 1 to 2. The "*bearing*" of the third face from the first two decides at once which of the two points of intersection is the pole of No. 3 on the sphere. The poles of all the other faces are got by an exactly similar construction. When this has been done, we have on the globe a number of points which form a complete catalogue of the faces of the crystal. Similarly, the arcs connecting each pair of poles furnish a catalogue of the inclination of every single face to every other. Every face of the crystal cuts the sphere of projection in a circle having the pole of the face as centre. Let us take the poles of two adjacent faces, Nos. 1 and 2, and with a pair of compasses draw a circle round each of them

with a radius which is greater than half the arc between the two poles. These circles cut each other. Let the points of intersection be joined by the arc of a great circle. That arc is the projection on the sphere of the edge produced by the intersection of the two particular faces, the normal radii of which we have assumed to be equal.

When the lengths of the radii are taken in any other ratio than that of equality the position of the edge is shifted, but its direction remains the same. It is always perpendicular to the plane containing the normals to the faces, which form it by their meeting. Therefore the great circle which is the projection of the edge is at right angles to the great circle drawn through the poles of the two faces forming the edge, and the direction of the edge is the direction of the axis of this great circle. If we imagine the edge to be carried parallel to itself until it reaches the centre of the sphere, it will coincide with the diameter which is the axis of the great circle in which the poles of the faces lie. Let the points where this axis pierces the surface be marked on the globe. They fix the direction of the edge of the two faces, and of all parallel edges.

When this construction has been repeated for every pair of adjacent poles on the sphere, we have the projections of all the edges as arcs of great circles. And if they have been all carried parallel to themselves to the centre of the sphere and their extremities then marked, we have another series of points which catalogue the edges just as the poles do the faces of the crystal. One diameter of the sphere represents all the edges of the crystal which are parallel to it, therefore the number of the diameters which have been thus entered on the globe is the number of the different or independent edges of the crystal.

We have here considered the edges formed by the meeting of adjacent faces, or the actual edges occurring on the crystal or polyhedron under measurement. But when every face is marked on the globe by its pole, it is equally easy to determine the direction of the edge which would be formed by the meeting of two faces which are remote from one another; so that, just as we were able, by measuring the arc between every pair of poles, to catalogue the inclination of every face to every other whether adjacent or remote, so we are able to lay down and catalogue the direction of every edge made by the meeting of every face with every other however they may be situated relatively to each other.

Again, the diameters representing the edges parallel to them all cut one another in the centre of the sphere. The

arc connecting the similar extremities of any pair of such diameters measures the angle included between them, which is equal to the *plane angle* included by them as edges of the face which they assist to delimit. In this way we obtain a catalogue of all the plane angles occurring on the faces of the crystal; and they are derived by a simple graphical construction from the observed inclinations of the faces. Further, the diameters representing the edges which bound one face all lie in the same plane; therefore the extremities of such diameters lie in one great circle. By drawing great circles through all the groups of diameters lying in the same plane, we get a group of great circles, each of which represents the intersection with the sphere of a plane which passes through the centre of the sphere and is parallel to the face of the polyhedron, which is bounded by edges parallel to the diameters which lie in the plane, and the extremities of which are connected by the great circle. We have thus a catalogue of the faces of the crystal which are inclined to one another, and the inclination of any two of the great circles measures the inclination of the pair of faces. Also the diameters marked as meeting the surface of the sphere in the great circle supply the number and direction of the edges which bound the particular faces (where it must be remembered that parallel edges are represented by the same diameters) and the plane angles of the face are given by the angles between the diameters. The representation of the faces of the crystal by great circle planes and that of the edges by diameters, all of which necessarily meet in the centre, facilitates the choice of a suitable system of crystallographic axes.

If we consider the poles of three adjacent faces, Nos. 1, 2, and 3, and draw small circles round them, the radii of which are equal, and of such a length that each circle cuts the other two, then, as before, we have the projection of each edge represented by the arc of the great circle connecting the intersection of each pair of circles. These three arcs cut one another in a point inside of the triangle formed by the insection of all three small circles. This point is the projection or pole of the *corner* formed by the meeting of planes 1, 2, and 3. If this corner be carried parallel to itself to the centre, its bounding edges will coincide with their parallel diameters, which thus form representative parallel central corners. These diameters meet the sphere in the extremities, which have been already fixed. If these points be connected by arcs of great circles, they determine a spherical triangle whose area is a measure of the corner.

By a well-known rule the excess of the sum of these angles above two right angles divided by four right angles, gives the area of the triangle as a fraction of the surface of a hemisphere. Corners delimited by more than three edges can be specified in the same way by splitting up the polygons which subtend them into triangles. The secondary figures thus described on the surface of the sphere are always different from the primary ones. Thus, the corners of the cube, when collected at, and radiating from the centre of the sphere, delineate the regular octahedron, which in its turn, when similarly treated, delineates the cube. It is a form of inversion.

It has thus been shown how the globe can be profitably used along with the goniometer. We have put no restrictions on the form of the polyhedron under measurement, and we have been able to render a complete account of the faces and their inclinations to each other, the direction of the edges produced by their meeting, and the plane angles produced by the meeting of pairs of edges. We have also been able to draw a complete and accurate representation of the polyhedron as projected on the surface of the sphere, which can be studied in detail. A collateral advantage which the student gains by using the globe in the study of crystallography or of solid geometry generally, is the excellent mental discipline which it affords. A very short training of this kind develops enormously the sense of direction. The greatest advantage is reaped by those who combine the use of the globe with the analytical treatment such as given by Miller in his treatise.

The globe offers great advantages for demonstration. It is very easy to draw correctly the projection of a crystal, especially when it belongs to one of the more symmetrical systems. In the regular system, for instance, which has the greatest number of simple forms, the edges between the faces of any of these forms are found at once when the poles of the faces have been laid down by drawing arcs of great circles at right angles to the great circle containing any pair of poles and midway between them. In this way an accurate representation of the crystal is quickly obtained. The curvature of the faces is not greater than is frequently met with in nature. Combinations of the simple forms can then be studied with advantage and in great detail. Further, hemihedral forms are as easily drawn as holohedral ones; more especially, twins, according to any law, can be *composed* and drawn on the globe as easily as simple forms. In short there is no operation in the geometry of crystals

which cannot with the greatest ease be performed by the use of the globe.

In bringing this matter before the Society I have not been concerned to produce anything very new or very original. It has been my object to draw the attention of other chemists to a method of studying Crystallography which I myself have found profitable. It is true that I had never seen a globe used in the study of Crystallography, nor had I met with any suggestion of its applicability. I looked through all the available crystallographic literature without finding any indication of it. When the projection on the sphere is mentioned, it is always with a view to dealing with it according to Miller's method by spherical trigonometry.

In May 1893 I gave a demonstration to the Philosophical Society of Cambridge (in connexion with globes generally) of the suitableness of black globes for studying crystals. When I began to prepare this paper I made a further thorough search through the literature, because I could not believe that the person who first had the idea to project the crystal on the sphere had done so with any other view than to study it when he had got it there. I could not meet with a copy of either Neumann's 'Beiträge zur Krystallonomie,' or Grassmann's work 'Zur Krystallonomie und geometrischen Combinationslehre,' which are alluded to in the beginning of Miller's Treatise on Crystallography, and I suspected that one or both of these authors might have recommended the use of the globe itself. A few days ago, through Messrs. Mayer and Müller of Berlin, I procured a copy of Grassmann's book. Its full title is 'Zur physischen Krystallonomie und geometrischen Combinationslehre.' Von JUSTUS GÜNTHER GRASSMANN, Professor am Gymnasium zu Stettin : Stettin, 1829. It is the first number of the first volume of a comprehensive work entitled 'Zur Mathematik und Naturkunde,' which the author proposed to complete by degrees. Nothing further was, however, published ; but the single number is a sufficiently remarkable work. It is worthy of note that he was obliged to publish it at his own expense, as it found no acceptance at the hands of the Scientific Societies or the Journals of the day. This is no doubt the cause why it produced so little effect in its time and is so difficult of access now.

Of Neumann's *Beiträge* also only the first fascicule appeared, and I have not yet been able to see a copy of it. I am informed that it is excessively rare. In Grassmann's work, however, the use of the globe is expressly recommended for presenting clearly to the eye and mind the combination of directions out of which he develops the systems of Crystallo-

graphy, and he states that one can make use of this instrument (the black globe) for solving by graphical construction all the problems of Crystallography, just as astronomical problems can be solved by the use of the celestial globe.

My expectation was therefore confirmed that the originator (if he was the originator) of the idea of projecting a crystal on a sphere, actually carried it out on a globe on which he made graphical constructions for the solution of problems and for the illustration of his subject. But Grassmann was not a crystallographer, he was a mathematician, and he deals with crystals mainly as affording interesting examples in nature illustrating a branch of pure mathematics, *die Combinationslehre*. The use of the globe in Crystallography proper, that is, starting from the crystal, is not dealt with at much length. His work received very little attention, and would probably have dropped entirely out of sight had it not come under the notice of Miller and suggested to him the treatment of the projection on the sphere by the methods of spherical trigonometry, which is now almost universally employed. It is to be observed that when the analytical work becomes too complicated and difficult on account of the want of symmetry of the crystal, there is no way of dealing with crystallographic problems except the geometrical, and the handiest geometrical method is the one very shortly described in this paper. For this reason also the use of the globe as a help in the study of Crystallography cannot be too strongly recommended.

Postscript, 24th June, 1895.

Examples.—In giving examples of the use of the globe in dealing graphically with the relations of the faces and edges of a crystal, it is necessary, to avoid unnecessary diffuseness, to make some conventions as to nomenclature. We call the *independent* faces and edges of a crystal, those that are inclined to one another; so that parallel faces and edges are represented by one independent face or edge. When we have placed the poles of all the faces of a crystal on the globe, we can represent *all* the faces by drawing suitable small circles round the poles, and we represent all the *independent* faces by drawing great circles round the poles. If we adopt the latter process one crystal is represented by a group of great circles, the plane of each great circle being parallel to the face or faces which it represents, and the points of intersection of any pair of great circles or their nodes mark the extremities of the diameter which is parallel to and represents the edge made by the pair of faces, and all other edges parallel to it.

The diagram produced on the globe by following the latter process will be called the *central representation* ; that obtained by the former, the *radial projection* of the crystal or polyhedron. The radial projection of a crystal when constructed with due regard to the length of the normal radii of the faces, and, consequently, to the exact position as well as to the direction of the edges, has the great advantage of affording to the eye a bodily presentation of the crystal, with all its irregularities of development. In the central representation the variability of the normal radii and, consequently, of the size of the faces, which distinguishes the crystal from the polyhedron, is effaced, and only the geometrical properties remain. The one process or the other will be adopted according to the purpose in view.

We shall designate the great circles representing the independent faces by numerals, 0, 1, 2, 3, &c., and the independent edges by the numbers of the two great circles which produce, by the meeting of their planes, the parallel diameter. Thus, the edge made by the meeting of faces Nos. 0 and 1 corresponds to the diameter made by the meeting of the planes of great circles 0 and 1, and it is designated edge (0, 1) ; similarly we have edges (0, 3), (1, 5), (2, 4), and the like. The position and inclination of a diameter is fixed when the point where it meets the surface of the sphere is known ; for it necessarily passes through the centre. It meets the surface in the node of the two great circles to which it is common. Hence the inclination or direction of the edge is given by the position of the corresponding node.

The nodes of intersection of the great circles will be designated by the numbers of the circles which meet in them, the opposite nodes being distinguished by a dash ('). Thus circles 0 and 2 meet in the nodes (0, 2) and (0, 2'), No. (0, 2) being the node which occurs first in azimuth, when travelling from node (0) along the equator in the direction which it has been agreed to call positive. Circles Nos. 1 and 3 meet in the nodes (1, 3) and (1,' 3') ; the former of these is situated in the hemisphere above circle No. 0, which is taken as the principal hemisphere of construction. Node (0, 1) being distinguished from the others by being made zero of azimuths, is called node (0), the node opposite it is called node (0, 1'). When the faces are represented by great circles, the inclination of any two is equal to the angle made by the plane of the one great circle with that of the other. They will be designated as angle (0, 1), (1, 2), and the like, the greater or smaller of the two supplemental angles being chosen according to the circumstances of the case. In order to fix the

position of the great circle, another element is required besides
its inclination to the great circle of reference or equator;
this is given by the azimuth of its node on great circle No. 0.
This also fixes the position of their common diameter and the
direction of the corresponding edge.   Hence the specification
of a great circle representing a face includes the specification
of the edge which it makes with the fundamental face of
reference No. 0, and also that of its equatorial node.   The
plane angle made on any one face by the meeting of two
other faces in it is equal to the angle between the diameters
formed by the meeting of the planes of the representative
great circles.   Thus, the plane angle formed in face No. 0 by
faces No. 1 and 2 meeting in it is equal to the angle between
the diameters formed by the intersections of the planes of
Nos. 1 and 2 with No. 0, and it is represented by the arc
of great circle No. 0 contained between nodes (0, 1) and
(0, 2).   Such angles will be designated by the numbers of
the three faces which are concerned in their production ; the
face containing the angle coming first.   Thus angles
(0—1, 2) (2—1, 3) mean the plane angle on face No. 0 made
by faces Nos. 1 and 2 and that formed on face No. 2 by faces
Nos. 1 and 3.   The great circle corresponding to the funda-
mental face of reference will always be called No. 0, and the
fundamental edge (0, 1) is the diameter made by the inter-
section of the planes of great circles Nos. 0 and 1.   One of
the nodes of these two circles, which will be called node 0, is
chosen as the zero of arcs of azimuth, which are measured
along great circle No. 0, from 0° to 360°.   Points lying out-
side of great circle No. 0, which is the equator of our system,
are further fixed by their altitude above or below it.   The
original position of the metrosphere means the one which it
had when great circle No. 0 was drawn and node 0 was marked :
then the equator of the metrosphere coincided with the
equator of the diagram on the globe, and the zero of azimuths
on the metrosphere corresponded with that on the globe.

In central representation, positions on the sphere are ex-
pressed by the azimuth from node (0) in which a great circle
passing through the pole of circle No. 0 and the point cuts
circle No. 0, and the arc on this circle contained between its
intersection with circle No. 0 and the point.   This is the
altitude of the point and it is + or − according as it is to
the right-hand or the left of the equator, when moving in the
positive direction of the measurement of azimuths.   The
coordinates of a point will be expressed shortly in the
form ($\theta°$, $\phi°$), where θ is the azimuth and ϕ the altitude.
The azimuth will always come first.   In central representation

a face is specified by giving the angle which the plane of the great circle which represents it makes with the plane of the equator, or great circle No. 0, and the azimuth of one of the nodes of intersection of the two circles. An edge is specified by azimuth and altitude of the node marking its extremity in the positive hemisphere. As it is a diameter of the sphere its direction is fixed.

As the measurements with the metrosphere used may vary to the extent of half a degree, angles and arcs whether observed or calculated are stated in degrees, and half or quarter degrees. It is impossible to illustrate examples without the aid of the globe itself, and the reader should have one before him in order to make for himself the construction described. The black or white globe with metrosphere mentioned in the paper is, on the whole, the best that is to be had in the market. The sphere Lejeune, to be had of the same publishers, is much more elaborate and admits of arcs being laid down and measured with greater accuracy and precision than the metrosphere of de Magnac, but it is less handy and costs four times the money. The handiness of the metrosphere is its great recommendation. One metrosphere can be used with any number of globes; so that separate details can be worked out on separate globes and combined on others, thus avoiding the risk of mistakes due to over-crowding. As extra globes for the metrosphere cost only ten francs each, the expense is small compared with the convenience afforded.

In the absence of a globe especially constructed for drawing, an ordinary terrestrial or celestial globe may be used with profit. It should be fully mounted, with complete brass meridian and wooden, or metal, equator, and should be furnished with a flexible brass quadrant to be attached to the meridian in the pole of the observer or elsewhere. If now the brass meridian be brought into such a position that the axis of rotation of the globe, which already lies in the plane of the meridian, comes to lie also in that of the equator, and the quadrant be attached to the meridian in the pole of the equator, we have an exact representation of the metrosphere, excepting that the circles in the ordinary mounting stand a little way off the globe, while those of the metrosphere touch and rest on it. The principal great circles such as the equator, ecliptic, and prime meridian are always clearly marked on a globe, and they are valuable as circles of reference. One of them is taken as circle No. 0. Great circles can be easily shown on the ordinary globe by pieces of twine or thin tape joined up at their extremities by an

elastic band.   If the tapes or threads are of different colours, the constructions made with them are very plain and easily followed.   A point may be marked on a varnished globe by attaching a small piece of gummed paper near its position, and marking the exact position on the paper with a pencil. Small circles, if they are wanted for themselves, are difficult to deal with ; but it is usually only intersections of pairs of them that are wanted and they are dealt with as points.   If the globe is kept fixed with circle No. 0 in the plane of the equator, points on its upper hemisphere can be laid down in altitude and azimuth by means of the flexible quadrant.   It will be seen, therefore, that an ordinary globe, even though its surface be not prepared for drawing on, can be used for the purposes of crystallography.   The terrestrial globe is to be preferred to the celestial, because on the latter the meridians are those of celestial longitude which meet in the pole of the ecliptic, while the axis of the globe passes through the poles of the equatorial.

As a first example let us consider the cube, because its details are so simple and so familiar that they can be easily followed without drawings and models.   If we place it on the goniometer and measure the inclination of its contiguous faces, we remark that they are all right angles, and we mark the poles on the globe in the way already described.   Let us now draw small circles round each pole, the radius of the small circles being sufficiently great for neighbouring circles to intersect.   If we then draw great circle arcs through each pair of intersections, we shall, after obliterating the small circles and other superfluous lines, have not only a correct projection of the cube on the sphere, but also a striking bodily presentation of it.   All the geometrical details can be studied on it.   No face is represented by a great circle, therefore, in specifying positions we have to take a great circle in a plane parallel to one of the faces for our equator of reference, and any point on it as the intersection with another face for the zero of reckoning.   We find, on examining our projection, that there are only three independent faces, and we can at once construct the central representation of the crystal by drawing great circles round the poles of the faces.

Place the metrosphere on the globe and draw the complete equatorial circle representing face No. 0 of the crystal. Mark on it the nodes of the meridian.   The one corresponding to 0° on the equator of the metrosphere is node No. 0, from which azimuths are measured.   The diameter connecting nodes No. 0 and No. $(0, 1')$ represents edge No. $(0, 1)$ which face No. 1 makes with No. 0.   From the specification of

the crystal the angle of inclination of these two faces is a right angle. Therefore in its *original position* the meridian of the metrosphere coincides with great circle No. 1. Let it be drawn. The third independent face, No. 2, which we find on the crystal is inclined to each of the other two at a right angle. With the metrosphere in its original position, clamp the movable quadrant at 90° of azimuth, the quadrant coincides with circle No. 2. It is generally more convenient to bring the meridian to coincide with the great circles to be drawn, because then the complete semicircle is drawn at once, and both nodes are marked at the same time. For this purpose the metrosphere is rotated from its original position round the axis of the equator, which remains coincident with circle No. 0, until division 90° of azimuth coincides with node (0, 1'). The meridian now corresponds with the position of circle No. 2. Let it be drawn. Circle No. 2 obviously cuts No. 1 at right angles, which can be at once verified by measurement of the arcs between node (1, 2) and nodes (0, 2) and (0, 2'). If we attempt to place any of the three remaining faces, we find that its place is already occupied by one of the circles, 0, 1, or 2, to which it is parallel. If we now wish to specify the crystal in terms of its central representation on the sphere, we have, for the inclination of the faces 0 to 1, $-90°$; 0 to 2, $-90°$; and 1 to 2, $-90°$; and, for the position and direction of the edges:—edge No. (0, 1) azimuth 0°, altitude 0°; edge (0, 2) $-(90°, 0°)$; and edge (1, 2) azimuth indeterminate, alt. 90°. The plane angle made on any face by any other two is equal to the arc on the corresponding circle contained between the nodes made by it on meeting the two other corresponding circles. In the present case they are found by measurement, as they are seen by inspection to be right angles.

In representing the cube by great circles parallel to its faces, we have divided the hemisphere into four equal and similar triangles. If we regard this diagram as the spherical projection of a polyhedron where *all* the faces, whether independent or not, are represented—where in fact the faces have been delineated by drawing small circles round their poles, and arcs of great circles through the intersections of these circles to give the edges, we find that we have here the radial projection of the regular octahedron. The transference of the faces of the cube parallel to themselves until they coincide with planes of great circles, has the effect of transferring the corners of the cube parallel to themselves to the centre. If the extremities of each set of three edges which go to form a corner are connected by arcs of great

circles, the diagram produced on the globe is the one which we have been considering. As was pointed out in the paper, the corners of the cube when radiating from the centre of the sphere delineate the projection of the octahedron on it. This fact can be expressed by saying that the central representation of the cube is identical with the radial projection of the octahedron.

Models exhibiting the central grouping of corners, and the forms thereby produced, are quite easily made out of cardboard or stiff paper, and are very instructive.

Let us consider the regular tetrahedron. The normals to its faces, four in number, are found to be inclined to each other at an angle of $109\frac{1}{2}°$ across an edge. The poles of these faces when placed on the globe form a group of four points symmetrically arranged, each being separated from its neighbour by an arc of $109\frac{1}{2}°$. Draw the great circles of which these points are the poles, and call any one of them No. 0. Take its intersection with any other and call it node (0), the opposite node is (0, 1′), and the great circle which intersects No. 0 in these nodes is No. 1, diameter (0, 1) being parallel to and representing the edge made by Nos. 0 and 1. Another pair of nodes are found in azimuth 120° and 300°. Their diameter represents the edge (0, 2), and the great circle represents face No. 2. Similarly the nodes of circle No. 3 are in azimuths 240° and 60°. The inclination of the faces is equal, and we find that the altitude of circles 1, 2, and 3 is $70\frac{1}{2}°$.

The edges (1, 2), (2, 3), and (3, 1) are found by measurement of the positions of nodes (1, 2), (2, 3), and (3, 1); node (1, 2) in ($330°$ and $54\frac{1}{4}°$); node (2, 3) in ($90°$, $54\frac{1}{4}°$); and node (3, 1) in ($150°$, $54\frac{1}{4}°$). The theoretical figures are here given because the observed ones have been mislaid. The errors, which did not exceed $1\frac{1}{2}°$, occurred in the quarter sphere of azimuth over 180°. This is always the case, because the metrosphere is never exactly true to the globes, and the errors show in proportion as it is shifted from its original position.

If we consider, as we did in the case of the cube, what form gives in radial projection the same diagram on the globe as the central representation of the tetrahedron, we find that it is the combination of the cube and octahedron " in equilibrium." The radial projection of each of its edges is an arc of 60°, and its principal sections are regular hexagons.

In the central representation of the tetrahedron let one of the great circles be suppressed. There remain three, and they constitute the central representation of the rhombo-

hedron, which consists of six rhombs with plane angles of 60°
and 120°.

When this diagram is looked on as a radial projection, it
is that of an octahedron in rhombohedral position, the two
basal faces being equilateral triangles, and the six prismatic
faces being isosceles triangles in which each of the equal sides
is double of the base.

Let us now consider the pentagonal dodecahedron as it
occurs in Nature as pyrites, and is designated by Miller
$\pi\{0\ 1\ 2\}$, and by Kopp $\frac{1}{2}(2a : a : \infty a)$. We shall consider
one face, which shall be represented by circle No. 0, and the
five contiguous faces, Nos. 1, 2, 3, 4, and 5, which by their
intersections give No. 0 its pentagonal shape. From the
specification or measurement of the crystal we have the
inclination of the normal of 0 to the normal of four of the
other faces 66° 25′·3 or $66°\frac{1}{2}$, and to the fifth 53° 7′·8 or 53°.
Let No. 1 be inclined to No. 0 at 53°, then Nos. 2, 3, 4, and
5 are all equally inclined at an angle of $66\frac{1}{2}°$. Place the
poles of these faces on the globe. Draw the great circles of
which they are the poles, then we have great circles Nos. 0, 1,
2, 3, 4, and 5 respectively parallel to and representing the
faces of the same number. We may also proceed directly to
draw the great circles. Place the metrosphere on the globe :
describe great circle No. 0 coincident with its equator, and
mark the nodes (0) and $(0, 1')$, also the pole of No. 0.
Clamp the quadrant at 90° of azimuth on the equator and
incline the metrosphere round the common axis of the equator
and meridian until the angle between the meridian and circle
No. 0 is 53°. The meridian is now in the position of great
circle No. 1. Let it be drawn, and let its pole be marked.
The two circles cut one another at an angle of 53°, and the
diameter $(0, 1)$ represents the singular edge of pentagons
Nos. 0 and 1.

By specification the inclination of faces 1 and 2 is $66\frac{1}{2}°$,
and equal to the inclination of 2 and 0 ; we have now to
place a third great circle on the globe, which shall cut
both the others at an angle of $66\frac{1}{2}°$. Clamp the movable
quadrant at an azimuth of $66\frac{1}{2}°$ on the equator. Bring the
quadrant to coincide with circle No. 0 and let it slide along
it. Then, if it is carried over the whole semicircle of No. 0,
the meridian must somewhere coincide with the position of
circle No. 2. While the quadrant is being slid along No. 0,
the pole of the meridian is describing a small circle parallel
to No. 0, which may be drawn on the globe. Now bring the
quadrant to coincide with circle No. 1 and let it slip along it,
marking the small circle parallel to No. 1 which the pole of

the meridian describes. The two small circles cut each other in one point in the hemisphere of construction. Now, with the quadrant coincident with No. 0, bring the pole of the meridian (90° of azimuth) to coincide with the intersection of the two small circles; the meridian coincides with circle No. 2. Similarly let the quadrant coincide with circle No. 1, and the pole of the meridian with the intersection of the small circles; then the meridian will be found to coincide with the circle No. 2 already drawn. In actual construction the coincidence was within half a degree. The method just described for finding the pole of No. 2 is inconvenient in practice. When the quadrant has been clamped at $66\frac{1}{2}°$ it is slipped along No. 0 to what appears to be a likely position, and the position of the pole of the meridian corresponding to it is marked on the globe. It is now applied to No. 1 at a likely place, and the position of the pole of the meridian corresponding to it is marked. If the first experimental position of the pole of the meridian be called a and the second b; then, from the pole of circle No. 0 with radius equal to the distance of a draw a small circle, it is necessarily parallel to No. 0; and from the pole of No. 1 with radius equal to the distance of b draw another small circle, which is necessarily parallel to circle No. 1. These are the same small circles as those above described, and the great circle described from their intersection as pole is necessarily identical with No. 2 already drawn. In making the construction on the globe the pole of No. 2 was found in this way. Small circles can be drawn with the metrosphere, but they are much more easily and accurately drawn with a pair of compasses. The position of the circle as drawn was proved by measuring the inclination of its plane to those of Nos. 0 and 1. The angle (2, 1) was found to be exactly $66\frac{1}{2}°$, and the angle (2, 0) was 67°. The arc or circle No. 0 contained between the nodes made by its meeting with Nos. 1 and 2 is equal to the plane angle on face No. 0 made by faces Nos. 1 and 2 meeting in it. By measurement on the globe it was found to be 101° instead of $102\frac{1}{2}°$. Similarly the arc between the nodes (1, 2) and (0, 2) is equal to the plane angle on face No. 2 formed by the meeting of faces 0 and 1 in it. It was found, on measurement, to be 122° instead of $121\frac{1}{2}°$. In the same way the arc between nodes (1, 2) and (0, 1), representing the plane angle in No. 1, was found to be 103° instead of $102\frac{1}{2}°$.

Great circle No. 0 being our equator of reference, and node (0), one of its intersections with circle No. 1, being our zero of azimuth, we have the positions of the faces and edges entered on the globe as follows:—

Face No.	1	2			
Edge No.	......	......	(0,1)	(0,2)	(1,2)
Azimuth	0°	102°	0°	77½°	288°
Altitude	53°	66½°	0°	0°	52°

These constructions were made with no greater care than is absolutely essential in carrying out any quantitative graphical work, and the plane angles agree within $1\frac{1}{2}$° of the theoretical values. With the very greatest care, errors of half a degree cannot be insured against with a globe of 22 centimetres and a metrosphere divided into whole degrees. With a larger globe and divided circles, especially adapted to this kind of work, greater accuracy could be obtained; but when the errors do not exceed one degree, the angles obtained are sufficiently exact to be used in the construction of models, which always forms the crucial test of the student's work on the globe or in crystallographic composition.

By an exactly similar construction we lay down circle No. 3 representing face No. 3, and on measurement we find for the positions of circle No. 3—$(151\frac{1}{2}$°, $65\frac{1}{2}$°), and edge No. (2, 3) (25°, 61°). When we now come to face No. 4, it is inclined to No. 0 at $66\frac{1}{2}$° and to No. 3 at 53°; we have therefore to find a great circle which cuts No. 0 at $66\frac{1}{2}$° and No. 3 at 53°.

The operation presents no more difficulty than when the angles were equal. The quadrant of the metrosphere is set to $66\frac{1}{2}$° and applied to circle No. 0; then it is set to 53° and applied to No. 3; experimental poles being marked in each case giving the radius of the small circles to be drawn from the poles of Nos. 0 and 3 respectively. The intersection of these circles marks the pole of the great circle sought, No. 4. The quadrant is now set either to 53° or $66\frac{1}{2}$°; if to 53°, then it is applied to circle No. 3 and slid along it until the pole of the meridian is in the intersection of the two small circles. The meridian of the metrosphere then coincides with circle No. 4, which is accordingly drawn. When the quadrant, set to $66\frac{1}{2}$°, is applied to circle No. 0 and slid along it till the pole of the meridian is again in the intersection of the two small circles, the meridian ought to coincide with the circle No. 4, already drawn. This construction was carried out and the resulting great circles fell less than half a degree apart. The coordinates of the plane are (209°, 66°). Circle No. 5 is inclined at an angle of $66\frac{1}{2}$° to both its neighbouring faces and is laid down exactly as No. 2.

After laying down the great circles Nos. 0, 1, 2, 3, 4, and 5, representing the fundamental face No. 0 and the five neighbouring ones, which by their intersections make No. 0 a pentagon, the positions and inclinations of faces and edges were taken off with the metrosphere. The measurements are along great circle No. 0 from one of its intersections with No. 1 as 0° of azimuth, and altitudes above or below it.

No. of face or great circle ...	1	2	3	4	5
Azimuth of node	0°	102°	$151\frac{1}{2}°$	209°	282°
Greatest altitude	53°	$66\frac{1}{2}°$	$65\frac{1}{2}°$	66°	66°

These are laid down directly from the data supplied for the crystal, and the small differences of the values thus found on the globe from those intended to be placed on it will give an idea of the precision to be obtained with the particular globe and circles. In the following table we have values derived graphically from this construction for the position and direction of edges formed by the meeting of any two of the faces represented on the globe by great circles. As before, the edges are represented by their parallel diameters, and these are designated by the nodes in which they meet the sphere. The azimuth and altitude of each of these nodes is given in the table. As the diameters also pass through the centre of the sphere, the edge is specified both as to direction and situation.

Node No.	1, 2	2, 3	3, 4	4, 5	5, 1
Azimuth	288°	25°	90°	156°	250°
Altitude	52°	61°	63°	$61\frac{1}{2}°$	51°

Node No.	1, 3	1, 4	2, 4	2, 5	3, 5
Azimuth	343°	109°	55°	270°	127°
Altitude	$23\frac{1}{2}°$	22°	44°	$24\frac{1}{2}°$	$43\frac{1}{2}°$

The first five of these edges actually occur ; the last five are the remaining possible edges which would be formed by the faces produced. They are shown on the globe exactly the same as the others, because, if a number of great circles be drawn on a sphere, every one of them bisects every other.

In the next table we have the plane angles on face No. 0

made by pairs of its contiguous faces. Here also we have
actually occurring and possible angles.

Nos. of contiguous faces ...	1, 2	1, 3	1, 4	1, 5	2, 3
Plane angle observed	103°	30°	27°	100°	107°
,, calculated ...	102½°	30°	29°	102½°	106½°
Excess	½°	0	−2°	2½°	½°

Nos. of contiguous faces ...	2, 4	2, 5	3, 4	3, 5	4, 5
Plane angle observed	50°	22°	123°	50°	108°
,, calculated ...	50°	25½°	121½°	50°	106½°
Excess	0	−3½°	1½°	0	1½°

If we suppose faces Nos. 1, 2, and 4 to be produced, they
meet in three edges forming a corner. The three plane
angles forming this corner are readily found on the globe.
They are the angles contained between the edges (1, 2), (2, 4),
and (4, 1) on the faces 4, 1, and 2 respectively. Hence we have
only to measure the arcs on great circles 4, 1, and 2 included
between their intersections with circles 1 and 2, 2 and 4, and
4 and 1 respectively; and by measurement they were found to
be :—plane angle on face 1, 108° ; on face 2, 72° ; and on
face 4, 75½°. Similarly, if we produce faces 1, 3, and 5 to
meet in a corner, the plane angles then are :—on face No. 1,
107° ; No. 3, 76° ; and No. 5, 74°. This is a group of
similar faces to the last. If faces 1, 3, and 4, a different
group, be prolonged they meet in a corner with plane angles
on No. 1, 59° ; on 3, 77° ; and on 4, 103°.

The interdependence between the plane angles of the faces
of a crystal and the inclinations of the faces and the edges
can be very conveniently studied on the globe.

Consider a face No. 0, as represented by its parallel great
circle on the sphere which shall be the equator of reference.
It is cut by any other face, No. 1, along a diameter one
extremity of which is taken as zero of azimuths. Let the
plane angle to be formed on No. 0 by faces Nos. 1 and 2 be
112°. Lay off on the great circle No. 0 an arc of 112°
azimuth ; the face No. 2 cuts No. 0, on the diameter of which
this point is an extremity.

Let the plane angles of 1 and 2 be equal and 112°, we have
to find their inclinations to No. 0 and to each other, and the
direction of the edge which they make with each other.

N 2

Set a pair of compasses to a span of 68°, which is the supplement of 112°, and with this radius describe small circles from adjacent extremities of the diameters (0, 1) and (0, 2). These circles cut each other in one point in the hemisphere. The position of this point is found by measurement to be azimuth 238°, and altitude 48½°. Through this point and the zero of azimuths (0°, 0°) draw a great circle which marks the position of the circle representing face No. 1. Also through the points (238°, 48½°) and (112°, 0°) draw a great circle which is parallel to face No. 2. The arcs intercepted on each great circle by the other two are 112°, and they represent the plane angles of the three faces meeting in the corner ; with the quadrant clamped at 90°, place the meridian on the points of intersection of No. 1 with Nos. 0 and 2, and the altitude of No. 1 is found to be 54°. By similar measurement the altitude of No. 2 is 54°. Therefore the faces 1 and 2 make angles with face No. 0 of 54° or 126°, according as the inside or the outside of the solid is considered. When the metrosphere is placed so as to measure the inclination of Nos. 1 and 2, it is found to be 53½°. The azimuth and altitude of the point of intersection of Nos. 1 and 2, which have been found by measurement to be 238° and 48½°, give the position and direction of the edge made by Nos. 1 and 2. The altitude 48½° is also the inclination of the edge made by two of the faces to the third face.

Let the plane angle on No. 0 be 120°, and the plane angles on Nos. 1 and 2 be 108° and 90° respectively. By exactly the same construction we find, on measurement, that the faces which fulfil these conditions are inclined 0 to 1 at 73½°, 0 to 2 at 58°, and 1 to 2 also 58°. The edge formed by Nos. 1 and 2 meets the sphere in 210° azimuth and 58° altitude. The plane angles here assumed are those of the square and the regular hexagon and pentagon.

If the edge made by Nos. 1 and 2 lies in azimuth 220° and altitude 50°, the base angle being 120°, to find the inclination of the faces and the plane angles of 1 and 2. Great circles are drawn through the points (0°, 0°) and (220°, 50°) giving circle No. 1, and through (120°, 0°) giving No. 2. The angles which they make with each other are then measured and found to be :—0 to 1, 61° ; 0 to 2, 50° ; and 1 to 2, 53½°. The plane angles are :—on No. 1, 118°, and on No. 2, 97°, the angle on No. 0 being given 120°.

The resources of the globe are inexhaustible ; but the above examples may suffice for the purpose with which this paper was written ; namely, to inform some, and to remind others, of the usefulness of the globe as an instrument of research.

XI. *On the Condensation and the Critical Phenomena of Mixtures of Ethane and Nitrous Oxide.* By Dr. KUENEN[*].

1. BEFORE relating the results arrived at in this investigation I shall have to give a short account of the course of thought which led to the choice of the subject.

My experiments on the conduct of mixtures[†] are based upon the theory of Prof. van der Waals[‡]. Van der Waals "describes" the properties of mixtures by means of an isothermal surface, the coordinates of which are the composition of the mixture x $(0 < x < 1)$, the volume v, and the free energy ψ ($\psi = \epsilon - t\eta$; $\epsilon =$ energy, $\eta =$ entropy, $t =$ temperature). On this surface there appear *plaits*[§], which determine the coexistence of two or more phases. Those points of these plaits which have a common tangent plane represent the phases which may coexist at the temperature for which the surface is constructed, and at a pressure indicated by the slope of the tangent plane $\left(p = -\dfrac{\partial \psi}{\partial v}\right)$. The double curves traced out by rolling the tangent planes over the plaits are the so-called *connodal* curves. It may happen that the plaits terminate on the surface itself (*i. e.* between the planes for which $x = 0$ and $x = 1$). In that case the coexisting phases approach each other and at last coincide in a so-called *plaitpoint*. In studying the plaits on the surface, one may use the projection upon the x–v plane. This projection consists of the x-axis between $x = 0$ and $x = 1$, the two v-axes for $x = 0$ and $x = 1$, the connodal curves with or without the plaitpoints. The points of the connodal curves belonging together may be joined by straight lines. The ratio of the parts into which these lines are divided by a line perpendicular to the x-axis, say for $x = x_1$, represents the ratio of the quantities of the two phases which will be formed when the mixture x_1 is taken at the pressure at which the two phases may coexist. Keeping this in view, it is easy to derive the condensation and critical phenomena of a mixture.

2. We shall only discuss the very simple case here, that

there is only one plait on the surface, the vapour-liquid plait, which determines the coexistence of a vapour-phase and a liquid-phase. The plait, roughly speaking, has the direction of the x-axis ; its plaitpoint, which will make its appearance if only we raise the temperature to a sufficient height, need not coincide with the end of the plait, *i. e.* with that point of the connodal curve which is nearest to one of the ψv planes (in the projection $= v$-axis). The latter point was called *critical point of contact*[*]. Now in deriving the critical phenomena two cases have to be distinguished depending on the relative position of these two points, which we shall call P and R. Either P is situated nearer to the ψx plane (x-axis) or this is the case with R.

3. In the first case the condensation of a mixture has the following character. Below a definite temperature (plaitpoint-temperature $= T_P$), different for every mixture, the quantity of the denser phase increases regularly during compression ; the pressure rises, and both the composition and the volume of both phases change continuously. Above another temperature (temperature of the critical point of contact $=$ critical temperature $= T_R$) there is no condensation possible. At temperatures ranging between T_P and T_R the condensation will have the following character :—With compression the quantity of the appearing liquid first increases, reaches a maximum value, and after that decreases till it disappears. This was called *retrograde condensation of the first kind* (r.c. I.)[†]. The nearer we get to the plaitpoint-temperature the larger becomes the quantity of the liquid and the smaller the difference between the phases, apparent from a less distinct liquid surface between the phases. A mixture, therefore, has a critical region instead of one critical point, lying between two critical temperatures.

4. The phenomena predicted in this manner were then observed by me in mixtures of carbonic acid and methyl chloride[‡], and afterwards of carbonic acid and air[§]. The deviation from what had been observed by former experimenters, viz., the flattening and disappearing of the liquid surface throughout the critical region without retrograde

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[*] Kuenen, *Archives Néerl.* xxvi. p. 379 ; Communications from the Lab. of Physics, Leiden, No. 4, pp. 7 *sqq.* ; *Zeitschrift phys. Chemie*, xi. p. 44.

[†] Kuenen, *Archives Néerl.* xxvi. pp. 378–379 ; Commun. No. 4 ; *Zeitschr. phys. Chemie*, xi. p. 44.

[‡] Kuenen, *Archives Néerl.* xxvi. pp. 382–385 ; Commun. No. 4 ; *Zeitschr. phys. Chemie*, xi. p. 47.

[§] Commun. No. 7, p. 6.

condensation, was explained by retardation[*], which was annihilated in my experiments for the first time by means of a small iron stirring-rod within the tubes, which was moved by an electromagnet outside the tubes.

5. If P lies on the other side of R there are again two definite critical temperatures, T_P and T_R, for every mixture; but the process of condensation between those two will be different from what it was in the first case. By compression a new phase appears of a larger volume[†] this time, *i. e.* a vapour-phase, which begins by increasing, then reaches a maximum, and then again diminishes and disappears. This was called *retrograde condensation of the second kind* (r.c. II.)[‡]. Near the plaitpoint-temperature T_P the liquid will be very flat and indistinct, and more so at the beginning than near the end of the condensation. Below T_P the condensation is normal.

6. This second case has never been realized till now. I have been considering whether it might be, and the choice of the subject of this paper is the outcome of my reasoning. In explaining this I shall use a different graphical representation, namely the p–t figure. In a recent paper[§] I have deduced the general features of the p–t curves in the problem before us from van der Waals's theory. The figure obtained consists of (1) the two *vapour-pressure curves* of the component substances; (2) the *border-curves*[||] for the mixtures ($x =$ constant) having the form of loops; (3) the *plaitpoint-curve*, being the envelope of the border-curves and connecting the critical points of the two substances. The point of contact between a border-curve and the plaitpoint-curve corresponds to the plaitpoint P of van der Waals's surface; the critical point of contact R is the point in which the border-curve has a tangent parallel to the p-axis. When going along the border-curve, starting from its lower branch, we may either first reach R or P. These two cases correspond to the

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[*] Kuenen, *Archives Néerl.* xxvi. pp. 376–377, 380–382; Commun. No. 4; *Zeitschr. phys. Chemie*, xi. p. 47.

[†] In order to make the volumes in our figures decide about the situation of the phases above each other, we should take the volume of the unit of weight as the unit of volume. In doing so a phase of larger volume is a lighter phase at the same time, and will therefore appear in the upper part of the tube.

[‡] Kuenen, *Archives Néerl.* xxvi. pp. 388–389; *Zeitschr. phys. Chemie*, xi. p. 45.

[§] Kuenen, *Kon. Akad. Amsterdam*, 29 Sept. 1894, pp. 90–99; 'Communications,' &c. No. 13.

[||] A border-curve for a mixture represents the conditions (p, t) in which it may coexist with a second phase.

two cases mentioned above. If P is situated beyond R we have r.c. I. (figs. 8, 9) ; if R lies beyond P we have r.c. II. (fig. 10). Keeping in view the connexion between border-curve and plaitpoint-curve, the question whether the second case can be realized comes to the same as whether the plait-point-curve or a part of it may rise, while the border-curves are situated on its left side (fig. 10). Now it appears that there are different cases in which such a situation must occur. If the critical points of some of the mixtures lie outside the critical temperatures of the two substances, a part of the plaitpoint-curve will answer to the above postulate. But this is not a necessary condition. If the substance of the higher critical temperature has at the same time larger vapour-pressures than the substance of the lower critical temperature, the plaitpoint-curve will have the same property. This case is represented in fig. 1. R lies beyond P. Between the

Fig. 1.
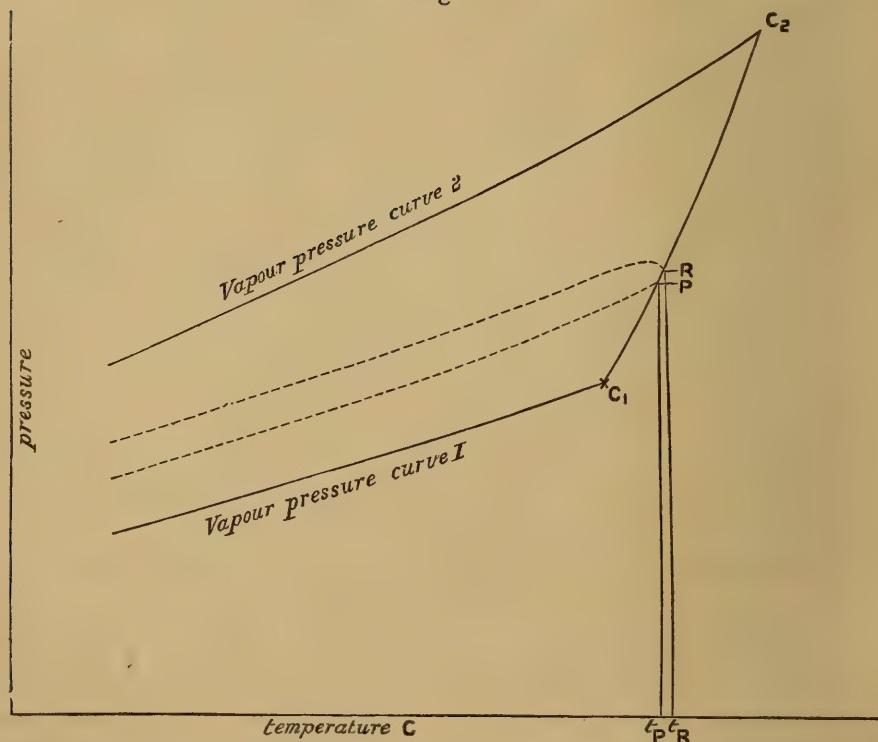
two temperatures T_P and T_R the mixture, the border-curve of which is drawn in the figure, must show retrograde conden-sation of the 2nd kind (r.c. II.). Even if the curves are more complicated than is supposed in the figure, the curve $C_1 C_2$ will nevertheless fulfil the condition at least for a part of its course.

7. There is only a small number of combinations of two

substances which appear to answer the purpose. Substances of low critical temperatures mostly have high critical pressures and high vapour-pressures. When this is not so, the differences are often too small to promise striking results. My attention was at last drawn to *ethane*, a substance of low critical pressure ($+50$ atm.) and a critical temperature of $+34°$ C. Combinations of this substance with HCl, C_2H_2, N_2O, especially the last, promised good results.

For this combination I expected to find a case such as is represented in fig. 1. It will appear that my expectation has been surpassed in so far as these mixtures happen to offer some interesting properties which had never been observed and require a more complex representation than fig. 1. At the same time the phenomenon (r. c. II.), to find which was the starting-point of the investigation, has escaped observation till now.

Preparation of Ethane (C_2H_6).

8. The ethane was prepared by electrolysis of a concentrated solution of acetate of sodium. By this process a number of other substances are generated, especially CO_2, O_2, C_2H_4, and some esters[*]. The gas was washed in sulphuric acid and a solution of caustic soda, and collected in a big glass bottle (45 litres) again containing a solution of caustic soda. In this manner the CO_2 was absorbed entirely. By aid of a mercury compressing machine of Cailletet, which belongs to the set of apparatus of the Leiden Laboratory for experiments at low temperatures, the ethane was liquefied in a small copper vessel. In this operation it passed again through fuming sulphuric acid, caustic potash, and phosphoric anhydride. In order to expel the permanent gases, the liquid ethane was cooled by solid carbonic acid and made to boil. In filling the tubes the gas was afterwards taken from the liquid.

This method of purification at low temperature has been formerly applied by me to CO_2 and CH_3Cl[†].

Preparation of Nitrous Oxide (N_2O).

9. This substance was taken from a commercial bottle; it was led through high-pressure tubes containing chloride of calcium and caustic potash and afterwards dried over P_2O_5. The purification was conducted as in the former case. During the boiling of the liquid N_2O the tube could be connected

[*] Kolbe, *Lieb. Ann.* lxix. p. 279; Wiedemann, *Electricität*, ii. p. 574.
[†] Kuenen, *Archives Néerl.* xxvi. pp. 356, 359. Olszewski was the first to apply this method of purifying gaseous substances so far as I know.

with an air-pump, a sort of mercury-valve being interposed in order to prevent air from returning to the liquid.

Preparation of the Mixtures.

10. The substances thus purified could be mixed in any proportion by means of my mixing apparatus, for the description of which I refer to previous investigations*. At present the whole apparatus consists of glass and copper only : the exhaustion was effected by a mercury air-pump.

Method of the Observations.

11. For the observations I made use of Ducretet's apparatus†. The glass tubes in which the gases were to be compressed were connected with the above apparatus by means of ground joints, and repeatedly exhausted and filled with the gases.

12. The temperatures, all of them ranging between 0° and 40° C., were obtained by means of a continuous current of water through a tube surrounding the experimental tubes.

13. My stirring apparatus‡, which was continually used during the observations, had been slightly modified. The little piece of iron with its knobs of enamel within the high-pressure tubes was the same as before; but the electromagnet, which used to slide over the tube and accordingly within the water-vessel, had been replaced by a larger bobbin sliding over the outside of the water-vessel. In this manner the influence of the temperature of the bobbin upon the temperature of the water, the constancy of which used to be disturbed during the acting of the apparatus, was removed. The bobbin is worked by four Bunsen cells or two accumulators.

Results obtained with Ethane.

14. In order to test the purity of the substances they were at first investigated separately. The gases appeared still to contain a little impurity : there was a slight increase of pressure during the process of condensation, for the ethane at 20°, 0·56 atmosphere. The amount of impurity of a gas corresponding to a definite increase of pressure at a definite temperature is difficult to decide, and entirely depends upon the substance itself and the admixture. In preparing the gas a second time, the liquid ethane was cooled in liquid ethylene boiling at a low pressure (−110° C.), itself being connected with an air-pump as in the case of nitrous oxide. The ethane obtained in this manner was found to be a little purer

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* Kuenen, *l. c.* p. 369.   † *L. c.* pp. 357, 366.   ‡ *L. c.* pp. 372 *sqq.*

still : the increase of pressure was 0·43 atm. at the same temperature *.

15. The critical temperature of the gases was determined very carefully : as with the mixtures, a stirring-rod had been put within the tube, and so the determination could be conducted according to the principles explained in the account of my observations with CO_2 †. The critical temperature for the two samples of ethane amounted to $31^c·95$ C. and $32°·05$ C. respectively. This would point to a critical temperature of $\pm 32°·3$ for pure ethane. By admitting a little air ($\frac{1}{4}$ to $\frac{1}{2}$ per cent.) into the last tube the increase of pressure at $20°$ C. rose to 2·7 atm., *i. e.* more than six times the former value ; while the critical temperature had gone down to $31°·25$ C. This would point to $\pm 32°·2$ C. as the real critical temperature of ethane. The admixture in my ethane seems to lie far below 0·1 per cent.

16. It is not impossible that, in filling the tubes, a little air remains in the gases, because they have to pass through some long tubes connected with joints before entering the experimental tube, and the air has to be expelled by means of exhaustion. I might probably have got a still purer gas by filling the tube more directly, but I preferred to apply exactly the same method which I used in preparing the mixtures, in order to be warranted against mistakes resulting from differences of purity.

17. The critical temperature of ethane as determined by former observers is somewhat higher. Dewar ‡ gives $35°$ C., Olszewski § $34°$ C., Haenlen ‖ from $32°$ C. to $40°$ C., probably $34°·5$ C. In his experiments retardation has played an important part, and his gas cannot have been very pure ; otherwise one finds a definite critical point, not a critical region as he does. He prepared the gas by the method of Gladstone, Tribe, and Frankland ¶ from C_2H_5I. Olszewski obtained ethane from C_2H_5Zn. Both Haenlen and Olszewski purified the gas by cooling and boiling at a low temperature.

I cannot tell what the reason is of this discordance between the values for the critical temperature. Perhaps it has some connexion with the different ways of preparing the gas. I am going to repeat the experiments with ethane prepared

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* Andrews, in his famous experiments on carbonic acid, observed an increase of pressure of more than two atmospheres in a similar case.

† Kuenen, *Kon. Akad. Amsterdam*, 29 Oct. 1893, pp. 85–90; Communications, &c., No. 8, pp. 11, 12.

‡ Dewar, Phil. Mag. [5] xviii. p. 214.

§ Olszewski, *Bulletin Ac. des Sciences de Cracovie*, 1889, p. 27.

‖ Haenlen, *Lieb. Ann.* cclxxxii. p. 245.

¶ J. Chem. Soc. xlv. p. 154; xlvii. p. 236.

from C_2H_5I. But the difference may be due to the method of determining the critical state as well. In my experiments the retardation is entirely annihilated by carefully stirring the gas, which may have lowered the critical temperature.

Results obtained with Nitrous Oxide.

18. Similar results were obtained with this gas. The increase of pressure, however, was still less. At 20° C. it amounted to 0·15 atm. = 11 cm. of mercury. The impurity of the gas may be estimated below 0·0002 : for the critical temperature I obtained 35°·95 and 36°·05. The true value will be 36°·1 C. probably.

19. Villard, who has prepared pure nitrous oxide by a similar process *, fixes the critical temperature of his gas at 38°·8 C. But this value was obtained by the indirect method of measuring the densities. The liquid surface disappeared below 38° C., but he does not mention an exact value. This gas must have been very pure, judging from the regular phenomena obtained near the critical point, and the purity of the carbonic acid prepared in the same manner. Villard states that in a U-tube in which two quantities of liquid N_2O were separated by a column of mercury, a pressure of a few centimetres sufficed to liquefy one of the portions completely. But this test is not so delicate as the one given above, viz. the entire increase of pressure from the beginning to the end of the liquefaction †.

20. The constancy of my results with the pure substances and the smallness of the admixture left, justify me in accepting an influence of the admixture upon the behaviour of the mixtures of a similar small amount.

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* Villard, *C. R.* cxviii. p. 1096; *Journal de Phys.* [3] iii. Oct. 1894. In a letter Dr. Villard tells me that his estimation of the critical temperature has been too high. In turning a tube with N_2O at 36°·5 C., the liquid surface disappeared and the tube filled itself with a blue mist. Now as stirring comes to the same as repeated turning, it is quite natural that I obtained a value for the critical temperature below 36°·5 C. I have not noticed the blue mist more than 0°·2 or 0°·3 above 36°·0 C. At any rate the disagreement between Villard's result and mine has been reduced to a few tenths of a degree. But it appears from Villard's measurements of the densities of N_2O, that the behaviour of this substance near its critical point is less normal, so to speak, than the behaviour of carbonic acid. One feels inclined to ascribe this to the influence of minute impurities.

† In filling a tube with a gas, which is compressed to a liquid afterwards, one works under unfavourable conditions for obtaining a pure substance compared to what can be obtained with liquids. The isopentane prepared by Prof. Young (Phil. Mag. [5] xxxviii. 1894, pp. 569–572) is remarkable in respect to purity. Here the increase of pressure appears to have disappeared entirely. Experiments by Battelli and others prove that even a pure liquid is not easily obtained.

Results obtained with the Mixtures.

21. The number of mixtures investigated was five. The composition (x parts of ethane in the volume in the gaseous state at one atmosphere) amounted to 0·18, 0·25, 0·43, 0·55, 0·76 respectively. The pressure and volume at the beginning and at the end of the condensation as observed at different temperatures are given in Tables I.–VII. The values of the volumes are only approximate. They are expressed in parts of the volume at 1 atm. and 0° C. For N_2O and C_2H_6 only one value for the pressures has been given. Tables VIII.–X. give the volumes for the temperatures 20°, 25°, and 26° C., as determined by graphical interpolation from the values observed.

TABLES I.–VII.

I.—N_2O.			
t.	p.	v_v	v_l
4·8	35·2	0·0206	0·6022
13·3	43·4	0·0161	
19·9	50·8	0·0125	
25·4	57·4[5]	0·0103	0·0027
31·5	65·4	0·0076	0·0031
36·0	71·9	0·0047	

II.—C_2H_6.			
5·85	27·4	0·0248	0·0033
10·65	30·4[5]	0·0215	0·0034
15·4	33·8	0·0184	0·0036
22·4	39·7	0·0140	0·0038
29·35	45·9	0·0103	0·0046
31·0	47·6	0·0089	0·0049[5]
32·0	48·8	0·0064	

III.—Mixture 0·18 C_2H_6.				
t.	p_1.	p_2.	v_v.	v_l.
2·85	35·34	35·55	0·0205	0·0026[5]
11·8	43·57	43·91	0·0143	0·0029
19·05	51·48	51·81		
23·2	56·40	56·57	0·0094	0·0031
29·8	65·32		0·0052 (?)	

IV.—Mixture 0·25 (?) C_2H_6.				
5·4	37·48	38·07	0·0177	0·0027
13·2	45·08	45·59	0·0131	0·0029
18·3	50·53	51·22	0·0111	0·0031
22·2	55·12	55·63	0·0094	0·0032
26·9	61·38	61·35	0·0066	0·0038
27·6	62·87	62·93	0·0065 (?)	0·0043
28·15	63·36		0·0046	

Tables (*continued*).

V.—Mixture 0·43 C_2H_6.

$t.$	$p_1.$	$p_2.$	$v_v.$	$v_l.$
9·8	40·59	......	0·0150	0·C030
14·3	44 96	45·57	0·0130	
18·6	......	......	......	0·0034
20·5	51·75	52·29	0·0096	0·C035
24·6	56·67	57 01	0 0073	0·0041
26 05	58·42			0·0055 (?)

VI.—Mixture 0·55 C_2H_6.

6·4	35·59	36·86	0·0195	0·0036
11·35	40·02	41 05	0 0164	0·0038
18·4	47·02	48·06	0·0126	0·0043
25·4	54·87	55·46	0·0084	0·0050
26 05	56·12			0·0069

VII.—Mixture 0·76 C_2H_6.

5·25	31·31	32·86	0·0217	0·0035⁵
12·4	36·99	38·54	0·0173	0.0037⁵
18·4	42·22	44·05	0·0140	0·0040⁵
21·95	45·81	47·05	0 0118	0·0042⁵
26·0	50·25	51·11	0·0092	0·0048
27·15	51·55	52·16	0·C083	0·0053
27·85	52·55			0·0066

Tables VIII.–X.

VIII.—Volumes at 20° (fig. 3).

$x=0·0.$	0·18.	0·25.	0·43.	0·55.	0·76.	1·0.
0·0125	106	102	98⁵	113	130	155
0·0025⁵	30	32	35	42⁵	41⁵	37⁵

IX.—Volumes at 25° (fig. 4).

0·0104⁵	87	78	70⁵	84⁵	98⁵	126
0·0026⁵	33	35⁵	42	48	45	40

X.—Volumes at 26° (fig. 5).

0·0101	85⁵	73	58⁵	69	92	99
0·0027⁵	34	37	51	58	48	47

The results are laid down in fig. 2, and figs. 3, 4, and 5.
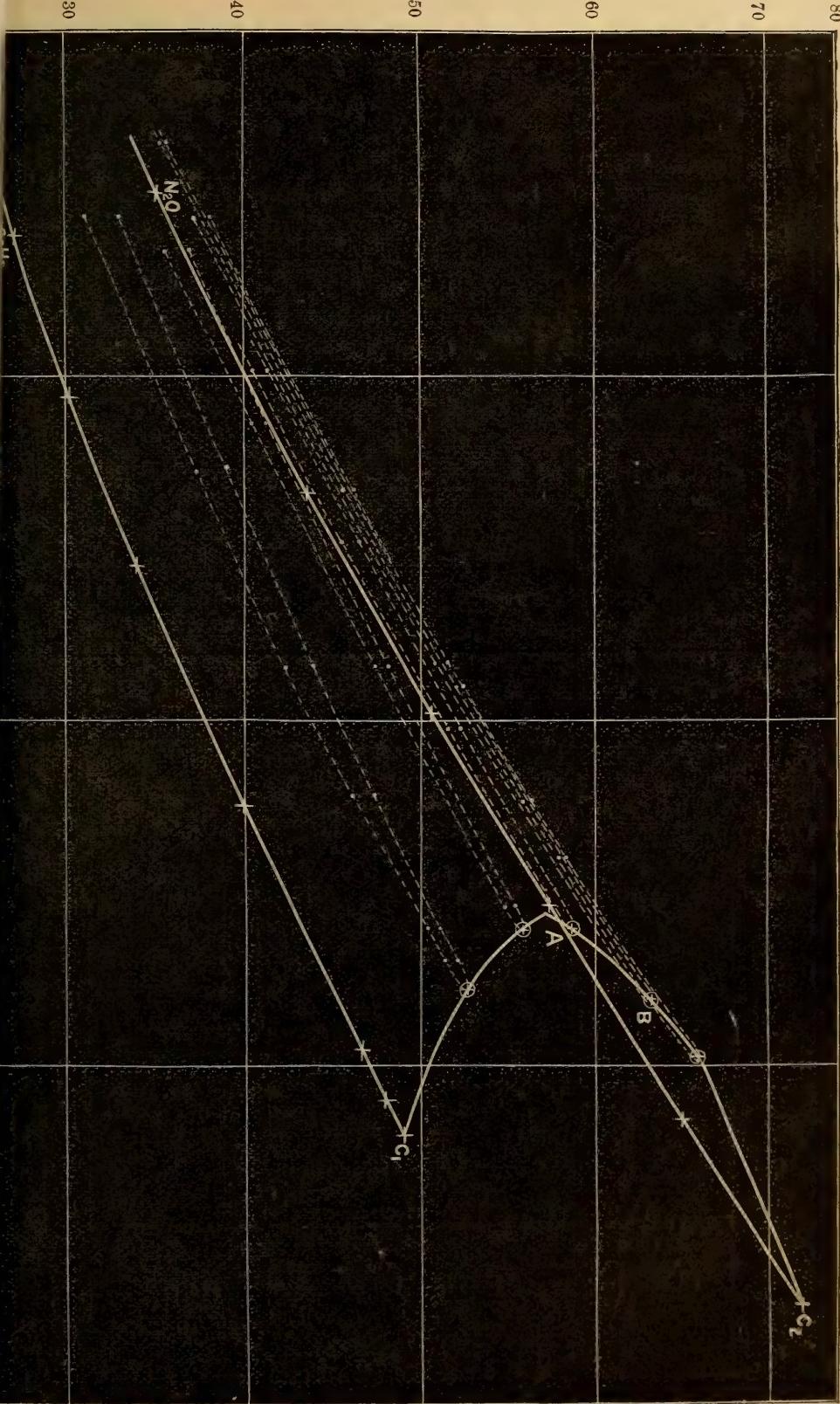
Fig. 2.

Fig. 3*. $t = 20°$ C.

Composition.
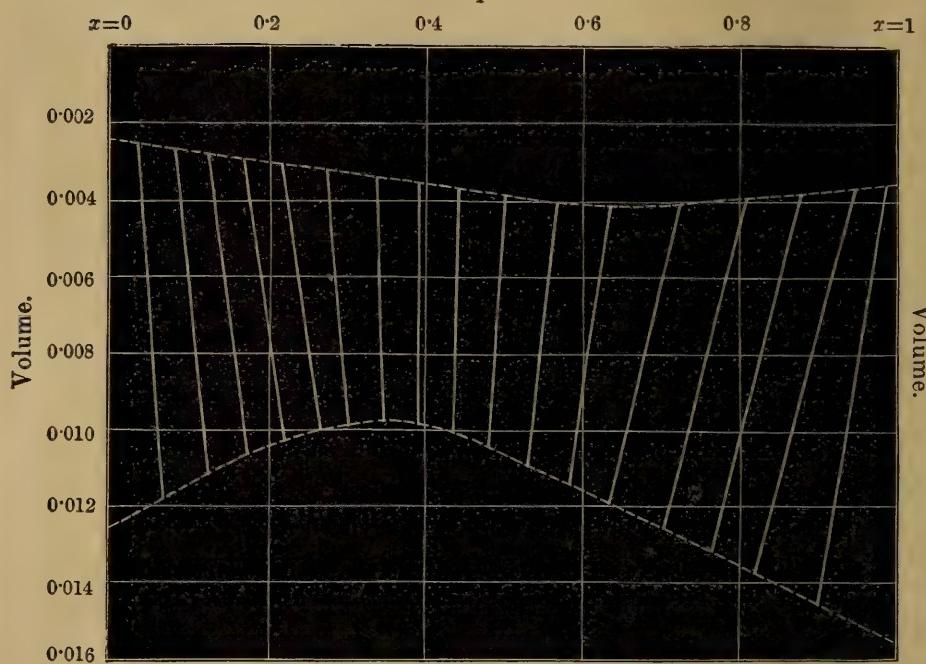
* There is a mistake in fig. 3 in so far as the straight lines near about $x = 0.2$ should be parallel to the γ axis, as in figs. 4 and 5.

Fig. 4. $t = 25°$ C.

Composition.
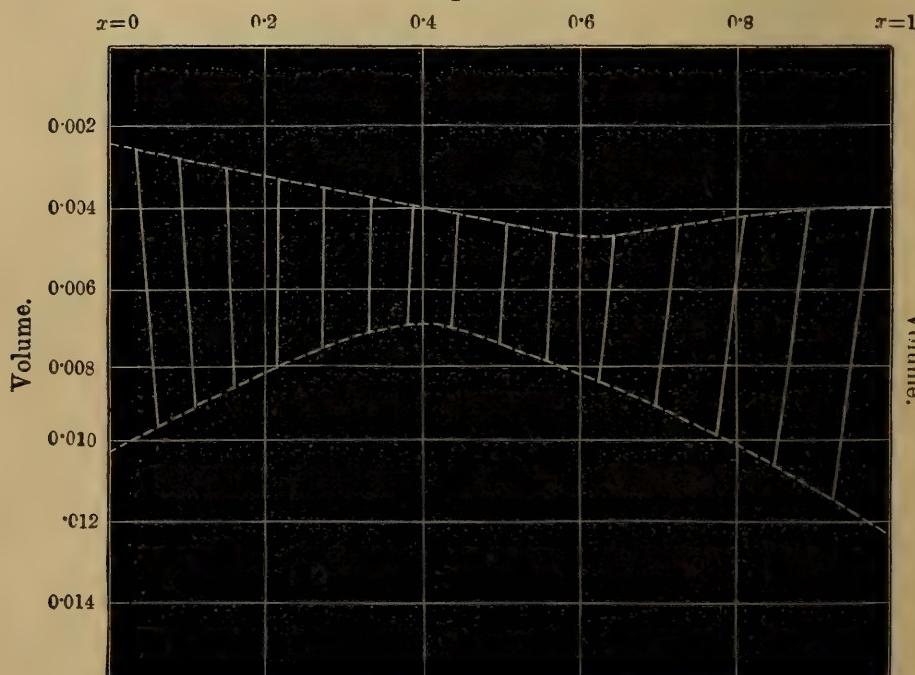
Fig. 5. $t = 26°$ C.
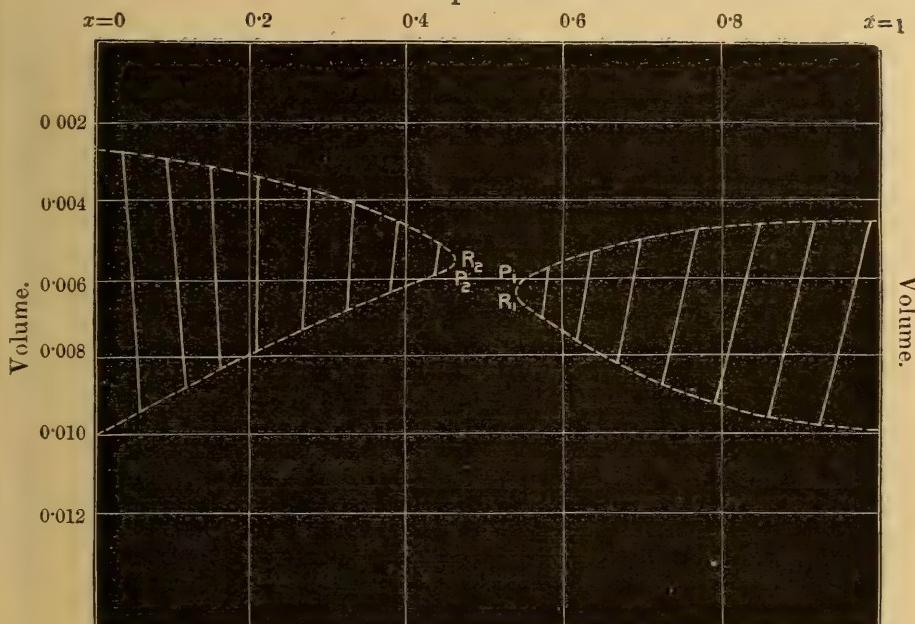
22. The axes of coordination in fig. 2 are p and t. This figure may be compared with fig. 1, which represented the curves as they would have been if the phenomena had been as little complicated as possible.

The curve $C_2H_6 - C_1$ is the vapour-pressure curve for ethane, $N_2O - C_2$ the same for nitrous oxide. C_1 and C_2 are the critical points. C_1ABC_2 is the plaitpoint-curve. The curves of the shape of loops are border-curves for the mixtures.

23. There are two striking differences between fig. 1 and fig. 2.

(1) The critical temperatures for a part of the mixtures lie below those for the components. By adding C_2H_6 ($32°$) to N_2O ($36°$), the critical temperature is lowered to a disproportionate extent. For a mixture containing $\pm 0·1$ of C_2H_6 the critical temperature has gone down as far as to $32°$, the c. t. for pure ethane. All mixtures containing more ethane than $0·1$ have critical temperatures below $32°$. Addition of N_2O to C_2H_6 therefore makes the critical temperature decrease instead of increase. The lowest critical temperature ($\pm 25·8$) belongs to a mixture containing $\pm 0·5$ of ethane.

A case like this has never been observed till now ; van der Waals's theory shows the possibility of the critical temperature lying outside those for the components[*].

* There is one instance of a mixture, the critical temperature of which lies *above* those for the components, observed by Dewar, namely, of CO_2 and C_2H_2 (Proc. Roy. Soc. of Lond. xxx. p. 543).

24. (2.) There is another difference between fig. 1 and fig. 2. The border-curves of the mixtures do not all of them lie between the vapour-pressure curves of C_2H_6 and N_2O. Some of them lie above the N_2O curve. It follows that at every temperature there is a maximum of pressure for one of the mixtures. From the figure it appears that this maximum lies somewhere between the mixtures the composition of which is 0·18 and 0·25, say ±0·2. The border-curves of the mixtures 0·18 and 0·25 differ only very slightly and in the figure almost coincide. The meaning of this is that the maximum belongs to almost the same mixture at all temperatures represented in the figure. If the mixture for which the pressure is a maximum varied quickly with change of temperature, the border-curves of the mixtures in that neighbourhood would intersect at perceptible angles. If we tried to draw the curve giving the maximum pressure at any temperature, it would lie a very little above the border-curves for $x=0·18$ and $x=0·25$, and be about parallel to those. This curve we shall call the *maximum-curve*.

25. There is another remarkable quality of the border-curves in this region near the maximum, viz. the narrowness of the border-curves, *i. e.* the very small increase of pressure during the condensation. The value of this increase amounts to 0·2–0·3 atm. for the first mixture, which is only a very little more than what still remained in the pure nitrous oxide itself[*]. We may therefore almost take it equal to zero. This agrees with what follows from the theory of mixtures. In a maximum-point (and also in a minimum-point) the two coexisting phases have the same composition (x) though different volumes (v), and there is no increase of pressure during the condensation. In order to determine the exact value of the maximum, a large number of mixtures lying about $x=0·2$ should be investigated : only the small admixture in the components themselves would of course impede the fixing of the maximum-curve.

26. In itself the existence of a maximum (or minimum)

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[*] The increases for the second mixture (0·25) are somewhat higher, viz. ±0·6 atm., which must be due to a somewhat larger impurity of that mixture. Probably the pressures of this mixture are therefore a little too high at the same time. The maximum will therefore be nearer to the first mixture (0·18). That is why I have put it equal to ±0·20. On the whole the values for the increase of pressure are a little irregular, which is quite natural considering the difficulty of these observations with mixtures. From the observations one might, perhaps, conclude that the maximum with rise of temperature shifts a little towards the N_2O; but as this seems rather uncertain, I prefer taking it constantly equal to 0·20.

pressure is not a new phenomenon. Guthrie[*], Konowalow[†], and others have found the same with different mixtures. Only, so far as I know, a maximum (or minimum) has never been traced up to the critical temperature. In Konowalow's mixtures the maximum appears sometimes to shift with change of temperature, and accordingly probably to disappear below the critical temperature. The above results prove that this need not be the case at all. This fact may be expressed in this manner : the maximum-curve need not reach the vapour-pressure curve of one of the substances. In my experiments it reaches the plaitpoint-curve, near B.

27. These results will be much better understood by inspecting figs. 3, 4, 5. The curves in these figures give the relation between the composition of the mixtures and the volumes at which the condensation begins and at which it ends (*vid.* § 1 *sqq.*), and may at the same time be considered as the projection of the connodal curves of the plait in van der Waals's surface upon the $v-x$ plane. The figures belong to the temperatures 20°, 25°, and 26° C. respectively.

28. If the phenomena were such as would correspond to fig. 1, the plait with rise of temperature would get narrower near the C_2H_6 plane ($x=1$). At 32° C. the curve would loose itself from the v-axis for $x=1$, whilst forming a plait-point there ; above 32° C. it would withdraw towards the N_2O axis ($x=0$), where it would disappear at 36° C. (critical temperature of N_2O).

29. However, this is not what really happens. With rise of temperature the plait becomes narrower somewhere near the middle. Consequently, at a temperature far below 32° C., near 25°·8 C., the plait divides into two parts. At that moment two plaitpoints appear (P_1 and P_2)[‡]. The two parts into which the plait is divided henceforth withdraw towards $x=0$ and $x=1$ separately. At 32° C. the right-hand plait disappears at $x=1$. At 36° C. the left-hand plait disappears in $x=0$. Above 36° C. there is no plait left : the surface is convexo-convex henceforth, and all its points represent stable phases.

30. A maximum pressure (or minimum) manifests itself in the $v-x$ figure in the position of one of the lines connecting

[*] Phil. Mag. [5] xviii. p. 510 *et sqq.*
[†] Wied. *Ann.* xiv. p. 34.
[‡] In two interesting papers (Wien. *Ber.* xcviii. pp. 1154–91; *Archives Néerl.* xxiv. pp. 57–98, 295–368) Prof. Korteweg has derived the geometrical properties of the plaits and plaitpoints. The case occurring here, viz. the formation of two plaitpoints of the same kind at the same time, is discussed on pp. 303–305.

the pairs of coexisting phases being parallel to the v-axis. The lines on both sides of the maximum line will be turned in opposite directions (with a minimum the direction in which the lines turn is the opposite of what it is here). But the angles of the lines are very small in the case of C_2H_6 and N_2O. On the right-hand plait the lines differ more: the increase of pressure is accordingly larger on that side of the surface. In the figure the turning of the lines had to be exaggerated in order to show their direction.

31. The critical phenomena of the mixtures were much simpler than I expected to find them. All the mixtures showed normal condensation up to the critical point, and a difference between plaitpoint temperature and critical temperature could not be determined with any certainty. The probable cause of this disagreement I shall refer to after having deduced more completely the theoretical consequences of the experimental results laid down in fig. 2, and figs. 3, 4, 5 (*vid.* §§ 43–46).

Theoretical Conclusions to be drawn from the Experimental Curves.

32. A. *Maximum-Curve.*—It may be proved that the border-curve of a mixture for which the pressure becomes a maximum touches the maximum-curve with both its branches. This is represented in fig. 6. In every point of the maximum-curve

Fig. 6.
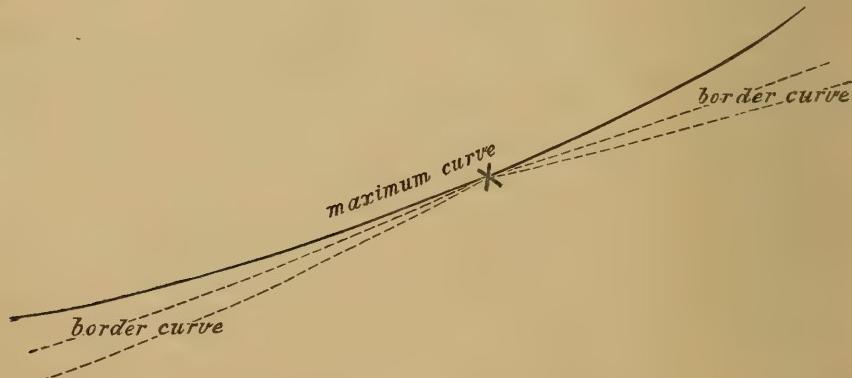
a similar meeting of three curves takes place. If the maximum-mixture does not change much with the temperature (as we found was the case with C_2H_6 and N_2O), the border-curve of the maximum mixture must have nearly shrunk to one curve coinciding with the maximum-curve.

33. Apparently the p–t figure is not at all convenient for showing the situation of the border-curves near the maximum-curve. The border-curves for the mixtures situated on

both sides near the maximum-mixture cover each other in
the figure. In a case like this it is much better to add as a
third axis of coordination the x-axis, and to draw the p-t-
curves for the mixtures each in its own plane. The curves
together in this manner form the p-t-x-surface. Sections of
the p-t-x-surface perpendicular to the t-axis again give
curves having the shape of loops (p–x-curves), which may be
considered as an extension of Konowalow's curves[*]: he only
gives the upper branches of the p–x-curves. A complete p–x-
curve is given by Prof. van der Waals in his treatise [†].

34. The maximum-curve meets the plaitpoint-curve in B.
Fig. 7 shows the manner in which the three curves (the

Fig. 7.
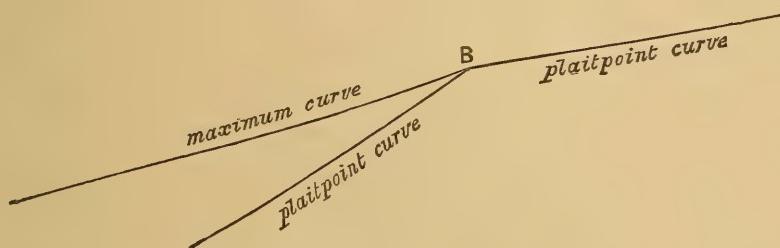
maximum-curve and the two branches of the plaitpoint-
curve) meet in B. It will have to be decided theoretically
whether, perhaps, the plaitpoint curve has no singular point
in B, in which case the maximum-curve would touch it in B.

35. B. *Critical Phenomena.*—The plaitpoint-curve (fig. 2)
consists of three parts, being situated between both the critical

Fig. 8.
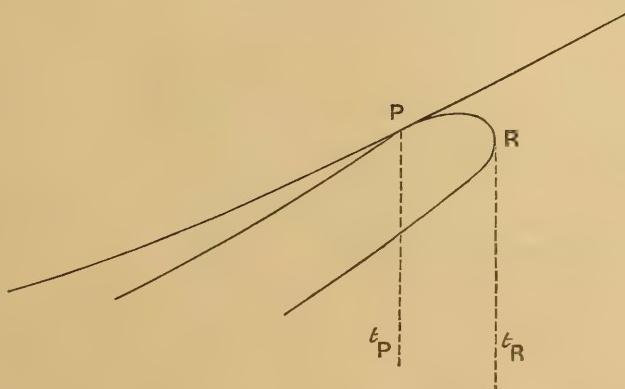
points C_1 and C_2, and separated by the two points A and B.
A is the meeting-point of two branches of the plaitpoint-

* Wied. *Ann.* xiv. p. 34.
† *Arch. Néerl.* xxiv. p. 21.

curve, where the critical temperature is lowest*.   In B the maximum-curve meets the plaitpoint-curve.

36. In the part C_2B the relative position of plaitpoint-curve and border-curves is like fig. 8.   P lies in the direction we called beyond R, and the border-curves touch the plait-point-curve on its right side.   The mixtures having their plaitpoint between C_2 and B, *i. e.* containing less than $0·2$ C_2H_6, therefore must have retrograde condensation of the first kind (r.c. I.) between the temperatures t_P and t_R.

37. In the part C_1A the curves are situated as in fig. 9. The border-curves lie on the left-hand side, but the plait-

Fig. 9.
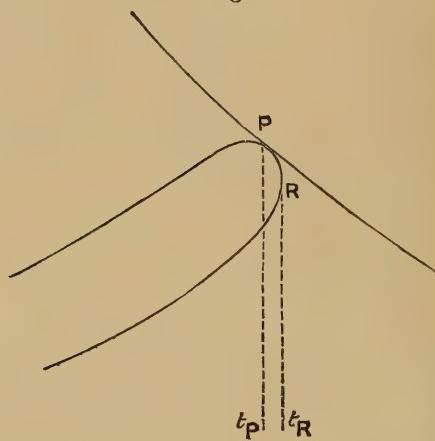
point-curve falls.   P lies beyond R.   The mixtures having their plaitpoint here, *i. e.* containing more than $0·5$ C_2H_6, must also have r.c. I. between t_P and t_R.

Fig. 10.
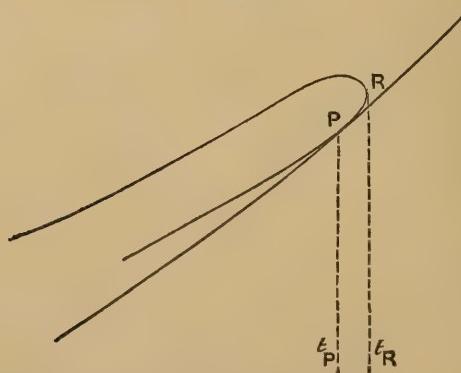
38. The part BA, however, fulfils the condition for the existence of r.c. II., as is shown in fig. 10 (*vid.* § 6).   The plait-

* The existence of a singular point in A was suggested to me by the experimental curves (fig. 2, *vid.* § 42).   Professor van der Waals, to whom I showed my experimental results, told me that he has theoretical

point-curve rises, and the border-curves lie on its left side. R lies beyond P. In this region lie the mixtures the composition of which is between 0.2 and 0.5 C_2H_6.

In consequence of the complexity of the curves as compared to fig. 1, the region of r.c. II. is a great deal smaller than it would have been according to fig. 1 (BA instead of C_1C_2). It is easy to see that this was the only thing which could happen : r.c. II. could not disappear entirely.

39. These rather strange conclusions are entirely made clear by figs. 3, 4, 5. These represent exactly the same phenomena, only in a different manner. If P lies above R we have r.c. I. ; if it lies below R, we have r.c. II. At first, after the dividing of the plait, the plaitpoints P_1 and P_2 lie on opposite sides of R_1 and R_2 in the two plaits. This corresponds to the existence of r.c. I. below A, and r.c. II. above A in fig. 2. While with rise of temperature the plait P_2R_2 shrinks together, R_2 approaches the maximum-line. P_2 approaches R_2 at the same time, and at the moment that the maximum reaches the end of the plait, P_2 and R_2 coincide. At that moment there is no retrograde condensation. The mixture $x = 0.2$ behaves at its critical point like a pure substance. P_2, however, now continues to move upwards, and henceforth lies a little above R_2. That explains the existence of r.c. I. between B and C_2. If there had not been a maximum, r.c. II. would have existed all the way from A to C_2.

40. The critical phenomena near the point where the plait divides into its two branches ($t = 25.8$, $p = 57.7$ atm.) are of a rather complex nature. This will be understood by the contemplation of fig. 11, where the two branches of the connodal curve at the moment of parting have been drawn on a much larger scale.

Let us consider the condensation of the mixtures x_1 and x_2 separately. It will be seen (*vid.* § 1) that the mixture x_1 in 1 begins to show a liquid phase which increases, decreases, and disappears in 2 (r.c. I.). Then, in 3, the liquid appears again, and in 4 the whole mixture will be liquid (normal condensation). Mixture x_2 liquefies in 1 : the liquefaction is at an end in 2 (normal condensation) : in 3 a vapour phase appears which disappears in 4 (r.c. II.).

---

reasons for believing that the plaitpoint-curve is continuous during its whole course, so that neither A nor B would be singular points. The conclusions drawn in §§ 40–42 and figures 11 and 12 entirely depend upon the existence of a singular point in A. There is, however, no connexion between those and the rest of this paper. Professor van der Waals will publish his results ere long.

41. Quite close to this temperature (below and above it) similar complicated phenomena will exist.   A little above

Fig. 11.
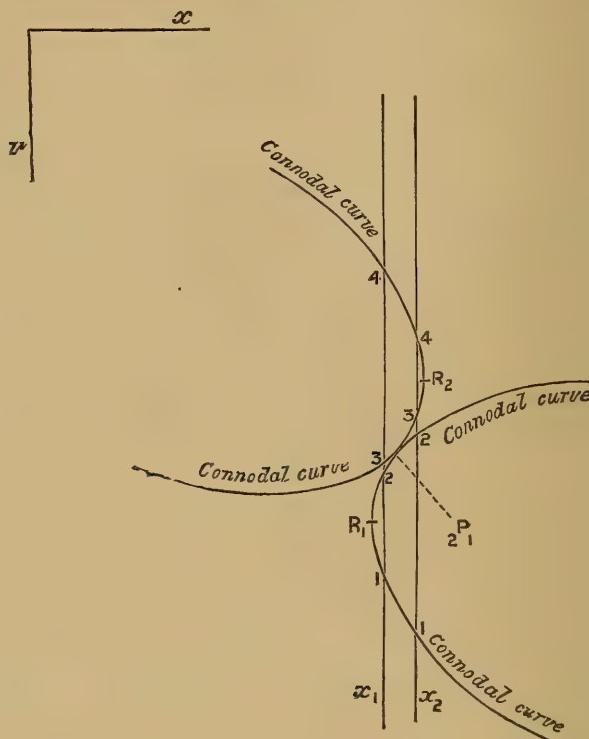
25·8 there are even some mixtures which show first r.c. I. and then r.c. II. successively with compression.   But as soon as the plaits have moved so far that there is no x-line cutting both plaits, the critical phenomena become the ordinary phenomena for a mixture (r.c. I. or II.).

42. The p–t-curves in the neighbourhood of A have a more complicated character, corresponding to the behaviour of the plait (fig. 12).   The two branches of the experimental plait-point-curve meet in a singular point.   The border-curves show a doubling, which disappears at a small distance from A.   A fuller explanation of the figure seems hardly necessary.   For clearness' sake only two border-curves have been drawn in the figure on an exaggerated scale.

43. How is it that in my experiments the mixtures did not show any of those critical phenomena partly of a so complicated nature, and almost behaved like pure substances near their critical points? (§ 31).   The reason lies at hand : I have pointed out the smallness of the increase of pressure, *i. e.* the approximate parallelism of the straight lines in fig. 3 (§ 30), and the exceeding narrowness of the loops (border-curves) in fig. 2 (§ 25).   Accordingly, as will be noticed in both figs. 2 and 5, the two critical points P and R lie close together, and

the distance between the temperatures of the plaitpoint and
the critical point of contact (t_P and t_R), for the same mixture,

Fig. 12.
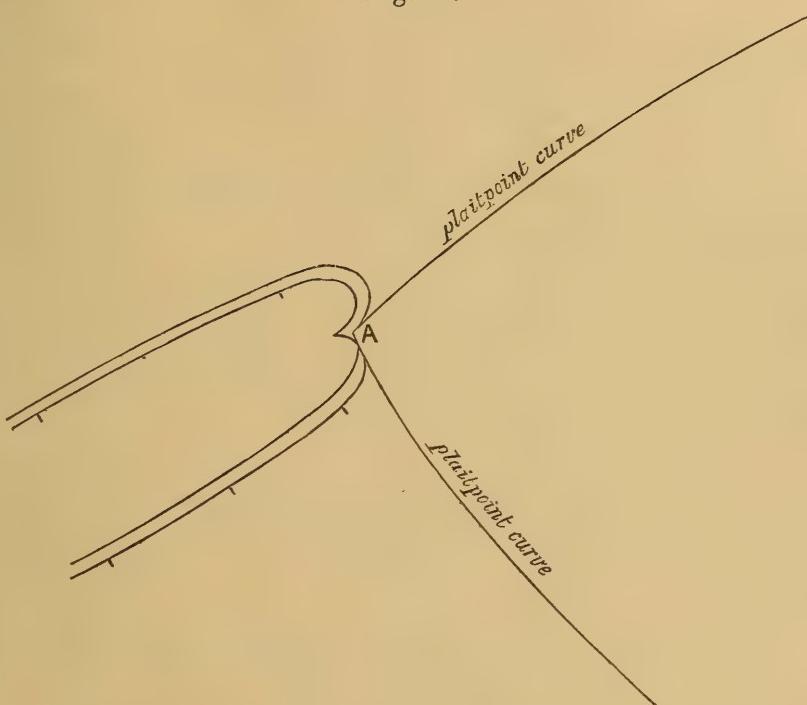
can be very small only.   An estimation from the original figure
2 gives $\pm 0°\cdot 1$ C. at the utmost for the distance between t_P and
t_R, and in some parts of the plaitpoint-curve—for instance
near B—much less still.   Now in order to fix so small a
difference the temperature ought to be perfectly constant for
a long while, which was not the case in my water-vessel.
There were slow changes, which of course did not prevent
the determination of the critical point taken as a whole.   I
think this circumstance may be taken as a sufficient explana-
tion of the disagreement between theory and experiments.

44. However, there is another cause which must have co-
operated in confusing the pure phenomena, viz. the influence
of gravitation.   It was Gouy[*] who, in the case of pure sub-
stances, first pointed out the importance of this factor near
the critical point, where the substances become so highly
compressible.   In the case of mixtures the influence of gravi-
tation is not of a quite simple nature.   The result is this :
near the plaitpoint there is a small region in which the com-
plete process of the condensation is confused ; namely in this
manner, that with compression at a certain moment the liquid
surface between the phases disappears at some distance from

[*] *Compt. Rend.* cxv. p. 720, cxvi. p. 1289; *cf.* Kuenen, ' Communications,
etc.' No. 8, p. 10.

the ends of the tube. In this manner the process of retrograde condensation is cut off halfway ; and if the distance between the two critical temperatures is very small, the phenomenon may perhaps disappear entirely [*]. This suggests the use of horizontal, or at least nearly horizontal, tubes for experiments on the critical phenomena.

45. Now in this region, where gravitation plays an important part, the stirring of the substance cannot be of any avail ; on the contrary, the equilibrium, which is very much influenced by gravitation, is spoilt rather by mixing together the different layers. So in this region the only thing we can do is, to wait a long time, and Gouy's experiments with an almost pure substance show that "long" means "days" here ; and of course that would be no use unless the temperature and the volume could be kept absolutely constant, which is practically impossible.

46. Though the special critical phenomena predicted by means of van der Waals's theory have escaped observation so far, there is no reason to doubt their reality or to see any contradiction between them and my experimental results, I believe.

47. Some of the results arrived at in this investigation may be enumerated here once more :—

1. The mixtures of C_2H_6 and N_2O containing more than 0·1 of C_2H_6 have critical temperatures lying beneath those of the substances (§ 23).

2. The pressures of the mixtures lie partly above those of N_2O, and accordingly show a maximum situated near 0·2 C_2H_6 (§ 24).

3. The maximum does not disappear with increase of temperature, but remains up to the critical region : the maximum-curve reaches the plaitpoint-curve (§ 26).

4. The mixtures ranging between 0·2 and 0·5 C_2H_6 have r.c. II., the rest r.c. I.

I intend now to investigate mixtures of acetylene and carbonic acid, a group of which according to Dewar[†] has critical temperatures lying above those of the components. If I should be able to confirm this result, I shall treat that combination in the same manner experimentally and theoretically as I have done the combination of C_2H_6 and HN_2O in this paper.

The experiments described in this paper have been carried out in the Physical Laboratory at Leiden, to the Director of which, Professor Kamerlingh Onnes, I am indebted for continuous and invaluable advice and help.

* Kuenen, *Verslagen kon. Akad. Amsterdam*, 25 Mei, 1895.
† Proc. Roy. Soc. of Lond. xxx. p. 543.

XII. *A Theory of the Synchronous Motor.*
By W. G. Rhodes, *M.Sc.**

[Continued from p. 63.]

Armature Reaction in a Single Phase Alternate Current Machine.

12. IN the foregoing analytical treatment the magnitudes only of θ, ϕ, and ψ are considered. We proceed to investigate the signs of these angles in order to determine the lags or leads of the E.M.F.'s over the current and to apply the results to find out whether the field excitation of generator and motor is strengthened or weakened by the reaction of the armature currents.

13. It will now be convenient to slightly alter the meanings of the symbols.

Let E = virtual value of generator E.M.F.
e = ,, ,, counter E.M.F. of motor (as before) ;
R = total resistance in circuit consisting of generator, motor, and line :
L = sum of coefficients of self-induction of generator and motor armatures; or, if the line possesses self-induction, the coefficient of self-induction of the whole circuit ;
I = impedance of the complete circuit ;
S = reactance of the complete circuit.

14. The E.M.F. Rc which drives the current is the resultant of E, e, and Sc ; so that E, e, Sc, and Rc reversed form a system of E.M.F.'s in equilibrium.

In fig. 3 let the positive direction of rotation be counter-clockwise, and let Oc be the direction of the current. The instantaneous value of the current does not concern us at present. Take OR' equal to Rc reversed, and consequently opposing the current; let OS' = Sc, lagging behind the current by a quarter of a period. The resultant, OT', of OR' and OS' will then be equal and opposite to the resultant of E and e. If, therefore, we produce T'O to T and make OT = OT', OT will represent in magnitude and direction the resultant of E and e. If, now, we are given the magnitudes of E and e we can find their directions by the parallelogram law. Now two parallelograms can be constructed having OT as diagonal

* Communicated by the Physical Society: read June 28, 1895.

and E, *e* as adjacent sides, but, since E is the E.M.F. of the generator, we take that which gives the component of E along

Fig. 3.
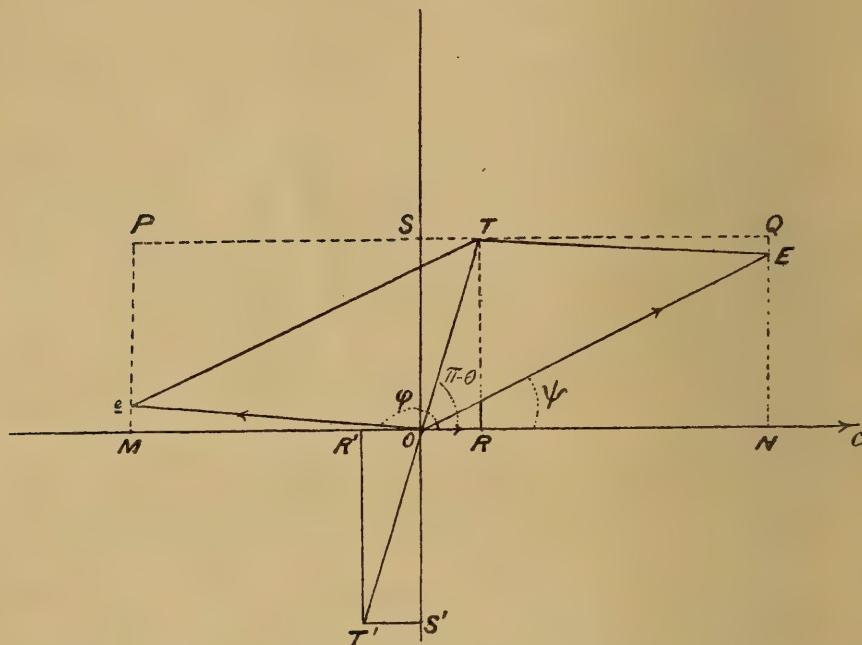
O*c* in the same sense as the current.   The other parallelogram would make *e* the generator.   We may notice that the possibility of constructing these two parallelograms affords a proof of the fact that, in general, either of two alternate current machines may be driven as a motor by the other, irrespective of their relative E.M.F.'s.   An analytical proof of this is given by the energy equation

$$p + c^2 \mathrm{R} = c\mathrm{E} \cos \psi,$$

remembering that

$$p = ce \cos \phi,$$

and that ϕ and ψ are independent.

The condition that E represents the generator E.M.F. limits our choice of the two parallelograms to OET*e* (fig. 3). We then have

$$\text{angle } c\mathrm{OE} = \psi,$$
$$\text{angle } c\mathrm{OT}' = \theta,$$
and
$$\text{angle } c\mathrm{O}e = \phi.$$

15. Now through T draw PSTQ parallel to the line of current, and draw PM, SO, TR, and QN through *e*, O, T, and Q respectively, at right angles to the line of current.

We have

$$\tan \theta = -\frac{Sc}{Rc} = -\frac{S}{R} = -\frac{2\pi n L}{R}, \quad . \quad . \quad . \quad (9)$$

that is, θ is independent of the current and OT is a fixed direction relative to Oc so long as the speeds of the machines are kept constant, and L is considered constant.

16. In fig. 3, OS (or PM) is proportional to the current, $[=2\pi n Lc]$;

OM is the component of e directly opposing c,

OR is the E.M.F. required to overcome resistance, $[=Rc]$;

and ON is the component of E in the direction of c;

hence, rectangle PSOM is proportional to the output of the motor $[p]$;

rectangle OSTR is proportional to the c^2R losses ;

and rectangle OSQN ,, ,, output of generator $[cE \cos \psi]$.

From this, and the equation

$$p + c^2R = cE \cos \psi,$$

it follows that the efficiency of transformation

$$= \frac{OM}{ON} = \frac{OM}{MR}.$$

17. If the output of the motor is kept constant, we have

rectangle PSOM = constant,

and the locus of P is a rectangular hyperbola having OM and OS as asymptotes (fig. 4).

Take any point P on this hyperbola. We have seen (9) that OT has a fixed direction relative to Oc ; and the point T (fig. 3) on this direction is found by drawing through P a line parallel to Oc. Again, e lies on the line through P parallel to OS and $eT = E$, in magnitude. Let the E.M.F. of the generator be kept constant and equal to E. With centre T and radius E describe a circle cutting PM in e and e' ; then the corresponding counter E.M.F. of the motor may be either Oe or Oe', and the current is represented in magnitude by PM : that is corresponding to given values of E and c there are two values of e. The relative phases in the two cases are shown in the parallelograms OeTE and Oe'TE' (fig. 4).

18. To find the point P' on the hyperbola corresponding to minimum current we have to bring the points e and e' into

coincidence.   The point P′ is obviously got by taking OE₁′
equal to E and through E₁′ drawing E₁′P parallel to OT.

Fig. 4.
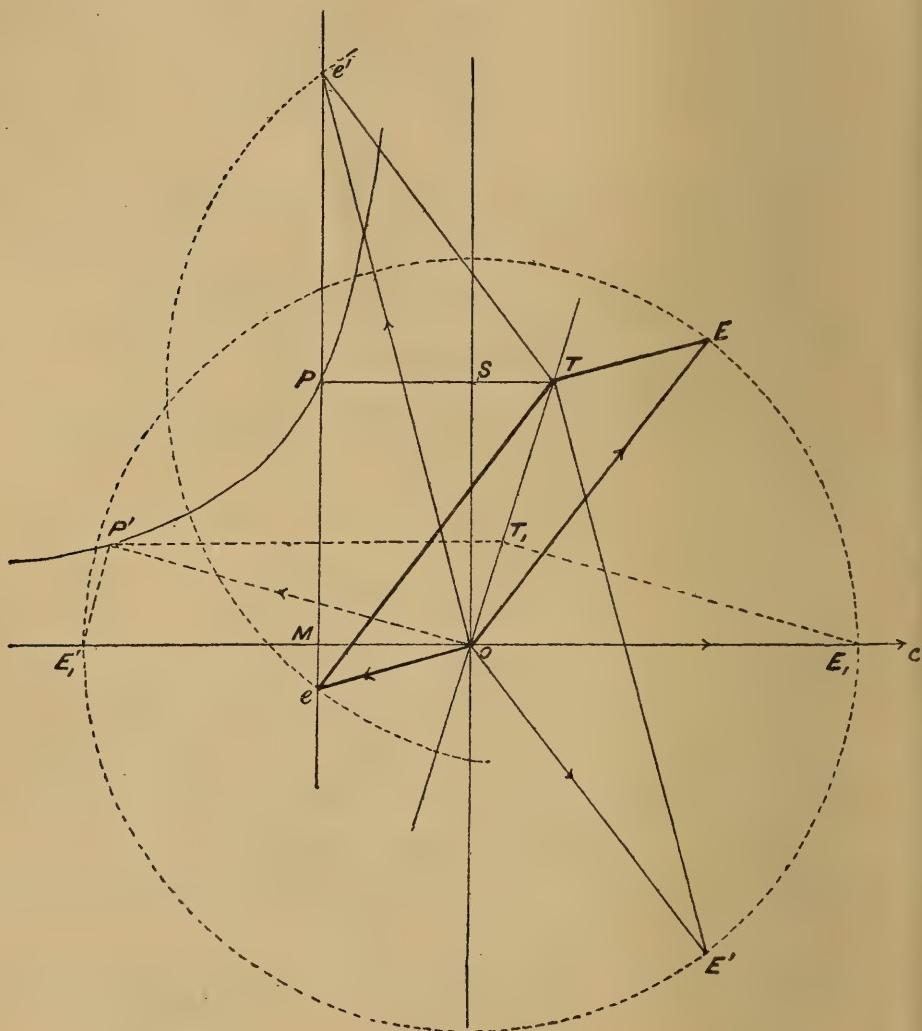
The resulting parallelogram OP′T₁E₁ shows that the generator
E.M.F. is in phase with the current.

19. Suppose now that the excitation of the generator field
is kept constant while that of the motor is varied.

When the motor excitation is small, as Oe (fig. 4), we see
that the current leads over the motor E.M.F. and lags
behind the generator E.M.F.

When e exactly opposes c, the latter lags behind E.

When E and c are in phase (minimum current), c lags
behind e.

When e is still further increased, as Oe', c leads before E
and lags behind e.

This explains the condenser action of an over-excited synchronous motor noticed by Professor S. P. Thompson and others.

20. It is known that a leading current strengthens the field of a generator and weakens that of a motor, while with a lagging current the reverse is the case. We therefore conclude that when the excitation of the motor field is small, armature reaction weakens the fields of both generator and motor, and when the motor is over-excited both machines have their fields strengthened. When working at minimum current, armature reaction strengthens the motor field and does not affect the field of the generator.

When the motor field is unaffected, the generator field is weakened.

21. Now the field of the motor is, under ordinary working conditions, excited to a somewhat greater extent than is required to obtain minimum current; for, though the c^2R losses are a minimum and the efficiency a maximum when the current is a minimum, it is advisable to increase the counter E.M.F. to a certain extent in order to cope with accidental variations of the load. Under ordinary working conditions, therefore, the effect of armature reaction is to strengthen the field of the motor and also of the generator, but to a less extent.

22. We now proceed to obtain an expression for the alteration, in ampere turns, of the field excitation due to armature reaction.

Let ϕ be the displacement of phase of the current over the E.M.F. of the machine ; n the number of turns of wire in one section of the armature; i the virtual current, and $i_0 \sin pt$ the instantaneous value of the current, so that i_0 is its maximum value.

It has hitherto been customary to assume that the alteration in the excitation is given by the expression

$$in\phi \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

where ϕ is expressed in circular measure.

Now it is not the *virtual* current to which the armature reaction is due, but the *mean value of the current* through an angle ϕ on each side of its maximum value ; that is, the proper value of the current is given by

$$I = \frac{p}{2\phi} \int_{\left(\frac{\pi}{2}-\phi\right)\frac{1}{p}}^{\left(\frac{\pi}{2}+\phi\right)\frac{1}{p}} i_0 \sin pt \, dt$$

$$= \frac{i_0}{\phi} \sin \phi.$$

And, remembering that $i_0 = \sqrt{2} \cdot i$, we get

$$I = \frac{\sqrt{2} \cdot i}{\phi} \sin \phi.$$

Thus the proper expression for the alteration of the field excitation in ampere turns is

$$2 I n \phi$$

or

$$2 \sqrt{2} \, i n \sin \phi. \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

To find the total excitation of the field we must add expression (11) to or subtract it from the ampere turns on the field according as the current leads or lags in a generator, and lags or leads in a motor.

XIII. *An Electromagnetic Effect.* *By* F. W. Bowden[*].

SOME time ago, under the direction of Prof. Perry, I was making some experiments suggested by Dr. Larmor. The following curious observations were made, and as Dr. Larmor thinks them distinct from his own object, I beg leave to bring them before the notice of the Physical Society. In fig. 1, N and S are nearly cubical blocks of iron whose edges are about 6 centim. long, forming the poles of an electro-magnet. The field between N and S near the middle was about 1100 C.G.S. A is the end view of a glass tube, 4 millim. internal diameter and about 30 centim. long, containing mercury and connecting two large mercury troughs, and a current of about 40 amperes was sent through it. A stand-pipe, B, 2 millim. diameter, indicated the pressure of the mercury. When the current passes in one direction (out from the paper) the mercury rises 15 millim. in B. When the current is reversed, the mercury falls 15 millim. Reversing the magnetic field produces the same effect as reversing the current.

With the tube in the position shown in fig. 2, the effects were of the same kind but not so marked, the rise and depression being about 10 millim. As the tube was lifted more and more out of the field, the effects became less and less.

The field being vertical as in fig. 3, the mercury *rose* in the stand-pipe when the current passed, and in whatever direction the current passed ; reversing the current did not

reverse the pressure-effect produced. Also reversing the field did not reverse the pressure-effect produced.

I again used a horizontal field as in fig. 4, the stand-pipe showing now the side-pressure in the tube parallel to the field. It was my intention to let fig. 4 really represent fig. 3 turned through a right angle, and again the mercury always rose in the stand-pipe, whatever the direction of the current or field.
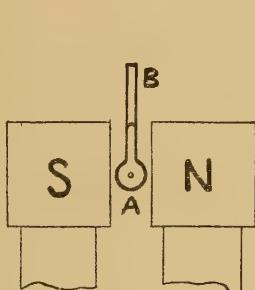
Fig. 1.
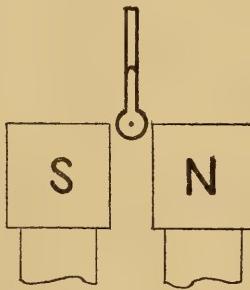
Fig. 2.
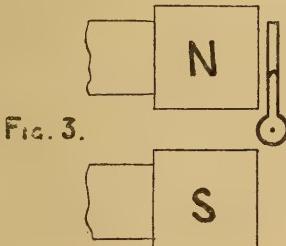
Fig. 3.
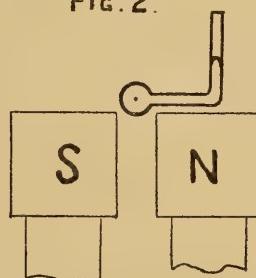
Fig 4
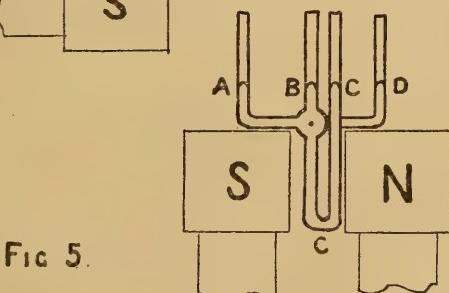
Fig 5.

Lastly, I let four stand-pipes communicate with the middle of the tube. The current passing in one direction, the mercury in B rose, in C fell, and in A and D rose only momentarily during the starting of the current. When the current was reversed, the mercury in B fell and in C rose, and rose momentarily in A and D.

The non-reversible effects of figs. 3, 4, and in the tubes A and D of fig. 5 are probably due to curious motions of the mercury, but it seems difficult to understand how. They do not occur when the tube is far away from the magnetic field.

XIV. *Determination of the Critical and the Boiling Tempe-rature of Hydrogen. By* Dr. K. OLSZEWSKI, *Professor of Chemistry in the University of Cracow* [*].

IN one of my previous papers[†] I have described a new method of determining the critical pressure of gases, which may be called the "expansion method," depending on the fact that a gas under high pressure and at a temperature not much higher than its critical temperature, assumes for a moment the liquid state when the pressure is slowly dimi-nished, this being manifested by the turbid appearance of the gas always produced when the pressure is lowered to the critical pressure of the gas experimented with. By means of this method I thus showed that the previously unknown critical pressure of hydrogen lies at 20 atm. In order to verify this method I tested it on two other gases, viz. on ethy-lene and oxygen, the critical pressures of which were accu-rately known. I also mentioned that, until we know of other cooling agents able to produce still lower temperatures than is possible by means of liquid oxygen or air, the expansion method will be the only one which allows us to determine not only the critical pressure but also the critical temperature of hydrogen. For if we could succeed by means of a very sensitive apparatus in determining the temperature of hy-drogen at the moment of its expansion to the critical pressure, at which the ebullition appears, this would doubtless be the critical temperature of hydrogen.

On again undertaking my researches, begun in 1891, I proposed to measure the temperature at the moment of the expansion of hydrogen by means of a thermo-electric junction, composed of very thin copper and German-silver wires. But several experiments performed in that direction soon proved that a thermo-electric junction is not suitable for such experi-ments, for the following reasons :—First, a junction composed of two wires soldered together can never be thin enough to assume instantaneously the temperature of the surrounding gas. Secondly, at very low temperatures the junction rapidly loses its sensibility, so that the deflexion of the galvanometer cannot serve to measure the temperature in agreement with the hydrogen thermometer. Then the measuring of low temperatures by means of a thermo-electric junction is possible

only between those limits in which it has been compared with the hydrogen thermometer ; every extrapolation would lead to quite false results.

After failing in my experiments with the thermo-electric junction, I resolved to measure the critical temperature of hydrogen by means of a platinum thermometer based on the variation of the resistance of a very thin platinum wire with the temperature. This method for measuring very low temperatures was proposed by Messrs. Cailletet and Collardeau*, afterwards also by Dr. Guillaume†, but practically it was used for the first time by Prof. Witkowski‡. His researches proved that the platinum thermometer is, after the hydrogen thermometer, the most suitable for measuring low temperatures. It is true that it demands an accurate comparison with the hydrogen thermometer, because the variation of the electrical resistance of platinum is not directly proportional to the variation of the temperature ; but between those limits in which it was compared with the hydrogen thermometer it may be used to determine low temperatures very rapidly and accurately. And considering that the curve which represents the relation between the temperatures measured with hydrogen and the electrical resistance of platinum is very nearly a straight line, we may draw the conclusion that by measuring very low temperatures by means of a platinum resistance-thermometer we may venture on an extrapolation to a moderate extent, and that the error which results from the imperfect agreement of the variation of the resistance to the variation of the temperature cannot surpass $0°\cdot5$ to $1°$.

The platinum thermometer of such a form as given by Prof. Witkowski is suitable for many practical purposes, but it does not follow variations of temperature with such a degree of quickness as is indispensable for the experiments I had to perform. The reason of the insufficient rapidity of Prof. Witkowski's thermometer is the not very thin platinum wire ($0\cdot06$ millim. diameter), which was insulated with silk, and hermetically enclosed between two concentric copper tubes made of very thin copper foil.

To give my thermometer the greatest possible sensitiveness I endeavoured to remove all that could have any contrary influence upon it. So, for instance, I used a much thinner wire of chemically pure platinum, whose diameter was only

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* *Journal de Physique,* 1888.
† *Archives d. Sc. phys. et natur. Genève*; also *L' Industrie électrique*, i. p. 78.
‡ Rozprawy (Transactions) of the Cracow Academy [2] iii. p. 380; Bull. Intern. of the Cracow Academy, 1891.

0·025 millim., and which was not insulated, and in consequence was able instantly to assume the temperature of the surrounding gas. The wire was wound in a spiral on a very delicate frame, made of ebonite or of very thin mica sheets, in such a manner that each single turn of the wire was 1 or 0·5 millim. distant from its neighbours and did not touch them anywhere. Nor was the wire coil enclosed in a copper tube, but it was in direct connexion with the surrounding hydrogen, and thus the rapidity of registration of the thermometer became considerably increased thereby.

The construction of the apparatus used to determine the critical temperature of hydrogen was on the whole the same as was used to determine the critical pressure of this gas, as described in the Philosophical Magazine (*l. c.*). I will therefore describe only those parts of the apparatus which were altered for these experiments.

So far as it was required to determine the critical pressure of hydrogen by means of an expansion method, we could not help using a glass vessel in which the cooled hydrogen was submitted to expansion from a high initial pressure ; for these experiments consisted in the observation of the pressure at the moment of the ebullition of the hydrogen, which could only be done in a transparent vessel. But after the critical pressure of hydrogen had been determined, a metal vessel could be substituted for the glass one. This change was advantageous for several reasons. It was possible to perform the experiments very quietly without any fear of an explosion, and without using masks or taking other precautions. The use of a metal vessel instead of a glass one allowed me to employ larger dimensions and to produce expansions from much higher initial pressures, and all this had a very great influence on the efficacy of the expansion and the precision of the measurement of the temperatures at the moment it took place.

The section of the apparatus serving to determine the temperature of the hydrogen during its expansion is represented in the subjoined diagram (fig. 1). In the steel vessel *a*, tested for a pressure of 220 atm., is placed a frame, *b*, of ebonite or mica with the platinum wire wound round it. Fig. 2 represents its vertical projection. One of the ends of the platinum wire is soldered to the tube *c* passing through the cover of the vessel *a*, and provided above with a binding-screw *d'* ; the other is soldered to the insulated copper wire *e* which passes through the tube *c*, in which it is closely cemented, and also provided with a binding-screw *d*. In the course of my experiments I used different frames, of various
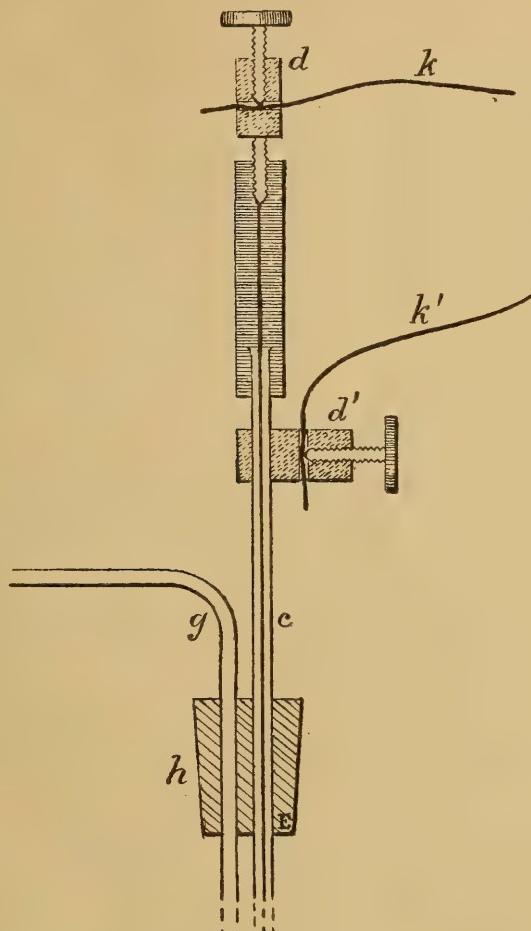
Fig. 1.

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Fig. 2.
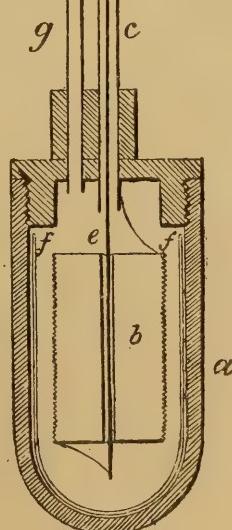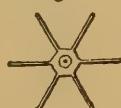
dimensions, sometimes of ebonite, sometimes of mica. In the first experiments I used an ebonite frame whose height was 20 millim. and diameter 12 millim.; the distance between the single turns of the wire was 0·5 millim., the resistance of the whole wire was 241·4 ohms at 0°. In a further experiment I used an ebonite frame whose height was 11 millim. and diameter 10 millim.; the resistance of the wire, which was wound also at intervals of 0·5 millim., was 117·5 ohms at 0°. In the final experiments I used a frame made of thin mica sheets: its height was 20 millim., the diameter 11 millim.; the resistance of the wire, wound in intervals of 1 millim., was 104·9 ohms at 0°. I devoted the greatest care to the construction of these frames; for the precise determination of the temperatures depended much upon their careful construction. I endeavoured therefore to make them of bad conductors of heat and electricity, and very light and with very thin wings at the edges where the wire touched them, so that the surfaces of contact were very small. The construction of the ebonite frames is easier, but those of mica are considerably less in mass; so that the larger ebonite frame weighed 0·679 gr. with the wire, the smaller ebonite with the wire 0·218 gr., whilst the mica one weighed with the wire 0·177 gr.; the wire of the latter weighed 0·011 gr., and was about 595 millim. long. The glass tube f with very thin walls which surrounds the frame b served to insulate it during the expansion from the warmer walls of the steel vessel a. The upper part of this vessel is screwed into it, and a close adhesion is produced by soldering it by means of an easily fusible bismuth alloy. The tube g serves to admit hydrogen, which is contained in a 3-litre iron flask under a pressure of about 170 atm. The lower part of the apparatus described is plunged in the liquid oxygen, whose temperature is lowered to about $-210°$ by pumping; the indiarubber stopper h serves to close the whole apparatus whilst the pumping is going on. The wires $k k'$ connect the apparatus with a Wheatstone bridge, for the purpose of measuring the resistance of the platinum wire wound on the frame b. To measure the resistance I used a very feeble current from one Leclanché element. This current was weakened by passing it through a resistance of 1000 ohms, to avoid heating the platinum thermometer; for the heating was distinctly to be perceived if this resistance was not brought into play.

The course of the experiment was as follows:—In order to draw the curve representing the dependence of the resistance of the thermometer on the variation of the temperature

measured with the hydrogen thermometer, I successively plunged the apparatus into melting ice, into a mixture of solid carbonic acid and ether, and into liquid oxygen boiling under atmospheric pressure and at a diminished pressure of 15 millim.; and I thus determined the resistances of the platinum thermometer at these low temperatures which correspond to $0°$, $-78°·2$, $-182°·5$, and $-208°·5$ respectively, according to the hydrogen thermometer. It is to be remarked that the temperature of the carbonic acid mixture ($-78°·2$) is constant only when the carbon dioxide is in excess, and when it has the consistence of butter : as soon as the ether begins to appear separately at the surface, the temperature gradually rises.

The variations of all the three platinum thermometers I used were quite proportional, and, calculated for 1000 ohms of resistance at $0°$, were as follows :—

Temperature according to the Hydrogen Thermometer.	Resistance of the Platinum Thermometer.
$0°$	1000 ohms.
$- 78°·2$	800 ,,
$-182°·5$	523 ,,
$-208°·5$	453 ,,

Thus for each $1°$ of the hydrogen thermometer between the limits

from $0°$ to $- 78°·2$ we have a fall of 2·557 ohms.
,, $- 78°·2$,, $-182°·5$,,   ,,   2·655   ,,
,, $-182°·5$,, $-208°·5$,,   ,,   2·692   ,,

This last number, viz. 2·692 ohms $=1°$, I used for the extrapolation in order to measure temperatures lower than $-208°·5$, at which the platinum temperature could not be compared with that of hydrogen. Assuming that the variation of the resistances is directly proportional to the variation of the temperatures below $-208°·5$, I committed an apparent error, which, nevertheless, cannot be great on account of the feeble curvature of the line of resistances ; for the temperatures extrapolated were not far distant from $-208°·5$.

To determine the resistance of the platinum thermometer at the moment of the expansion of hydrogen from a high pressure, I brought into the steel vessel a, cooled by means of liquid oxygen (at 15 millim. pressure), hydrogen under a pressure of 120 to 160 atm.; in the resistance-box I diminished the resistances, by which means the equilibrium was destroyed, and the galvanometer marked a considerable deflexion.

When the temperature of the hydrogen in the steel vessel became equal to the temperature of the surrounding oxygen, I made a slow expansion of the hydrogen to its critical pressure (20 atm.), if I wished to measure its critical temperature, or to the atmospheric pressure, if I wished to determine its boiling-point. As the cooling of the platinum wire during the expansion continued, the galvanometer returned to the zero-point, *if* the resistance in the resistance-box was chosen so as to be equal to the resistance of the platinum thermometer during the expansion. If in the first experiment the galvanometer did not return precisely to the zero point, I varied the resistances in the resistance-box, and repeated the experiment till that return took place. I thus performed six series of experiments : each of them was composed of about twenty determinations of the critical and the boiling temperature of hydrogen.

As already mentioned, I used in these experiments three platinum thermometers of different dimensions ; as cooling agents I employed liquid oxygen boiling under a pressure of 18 to 12 millim.; in one series of experiments I used liquid air, boiling under equally low pressure. The results I obtained were always the same, and relatively very much in agreement with one another, if we consider the great difficulty in performing such experiments. The mean numbers, calculated from many experiments, with reference to 1000 ohms at 0°, were as follows :—

Expansion of Hydrogen from a high pressure to	Resistance of the Platinum Thermometer.	Temperature Extrapolated.
20 atm. (critical pressure)	383 ohms.	$-234°{\cdot}5$ (critical temperature)
10 „	369 „	$-239°{\cdot}7$
1 „ (atmospheric press.)	359 „	$-243°{\cdot}5$ (boiling temperature)

On the basis of these numbers we can consider $-234°{\cdot}5$ as the *critical temperature*, and $-243°{\cdot}5$ as the *boiling-point* of hydrogen.

In a preliminary note, published in 'Nature'[*], I gave $-233°$ as the critical temperature, and $-243°$ as the boiling-point of this gas. These numbers do not differ much from

[*] 'Nature,' No. 1325, March 21.

those given now, and were based upon many careful experiments. Considering that the temperatures extrapolated must have been determined a little too low, for the reasons I have stated above, the numbers previously communicated may even be nearer the true data.

I showed above how the expansion method enables us to determine the dependence of the temperature upon the pressure of the gas liquefied, even though the cooling agents do not allow us to reach the critical temperature of the gas experimented with. It would be possible to make the following objections. First, we might ask how it is possible to know whether the gas, expanded from a temperature higher than the critical temperature, to a pressure of 20 atmospheres or of 1 atm., really assumes a temperature equal to the temperature of the liquefied gas, under one or other of these pressures. And then, if this were granted, whether the platinum thermometer described is rapid enough in its indications to assume and to mark the temperature of the surrounding gas at the moment of the expansion.

To ascertain whether these objections had any real foundation, I have done just what I did for the determination of the critical pressure of hydrogen, viz., I performed a series of analogous experiments with oxygen, whose critical and boiling points, and vapour-pressures at several different pressures I have determined in a former paper * , using the hydrogen thermometer. The experiments were performed in a similar manner, with this difference, that for the iron flask containing hydrogen under 170 atm. I substituted another flask, containing oxygen under 110 atm.; to cool the steel vessel containing the platinum thermometer I used liquid ethylene, boiling under atmospheric pressure ; then I cooled the oxygen, which was under a pressure of 100 to 110 atm., to a temperature which was about 16° higher than its critical temperature, and expanded it to 50·8 atm. (critical pressure), to 32·6 atm., to 19 atm., to 10·2 atm., and to 1 atm. The measurement of the resistances of the platinum thermometer was done more quickly in these experiments than in those with hydrogen ; for, knowing from my former experiments the relation between the temperature and the pressure of liquefied oxygen, I was enabled to determine beforehand with very near approximation the resistances which ought to be inserted in the resistance-box.

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* Rozprawy (Transactions) of the Cracow Acad. [1] xiii. p. 27 ; also *Comptes Rendus*, c. p. 350 (1885).

The results of this experiment are contained in the following table :—

Pressure of the Oxygen.	Temperature of Liquid Oxygen determined by means of a Hydrogen Thermometer.	Temperature of Liquid Oxygen determined by means of the Expansion Method.
50·8 atm. (crit. press.)	−118°·8 (crit. temp.)	from −118° to −119°·2 (crit. temp.)
32·6 ,,	−130°·3	−130°
19·0 ,,	......	−140°·5
10·2 ,,	−151°·6	−152°
1·0 ,,	from −181°·4 to −182°·7 (boiling temp.)	from −181°·3 to −182°·5 (boiling temp.)

This hardly expected agreement of the results obtained by means of both methods shows that the objections we have stated above are not justified, and that the expansion method is quite suitable for determining the critical and the boiling temperatures of gases.   The agreement of these results was doubtless also strengthened by the circumstance that the temperatures of oxygen had not been extrapolated, but were calculated by interpolation.   The initial temperature of oxygen was, it is true, only 16° higher than its critical temperature, while the initial temperature of hydrogen was about 26° above its critical point; but I endeavoured to compensate the untoward influence of that circumstance by using a much higher pressure, surpassing by 50 to 60 atm. the initial pressure used in the experiments with oxygen.

In conclusion, I must mention that my colleague Prof. L. Natanson has shown that the expansion method which I have used and described here can be justified theoretically on the basis of thermodynamic considerations*.   Shortly before I performed these experiments, Prof. Natanson also calculated and published the probable critical and boiling temperatures of hydrogen† on the basis of the law of corresponding temperatures, and the numbers given by him are sufficiently in agreement with those experimentally found by myself.

* *Bullet. Intern. de l'Acad. de Crac.* April 1895, p. 130.
† *Ibidem*, March 1895, p. 93.

XV. *The Velocity of Electric Waves.*
By John Trowbridge *and* William Duane[*].

THE direct determination of a velocity implies the measurement of a length and of a time. So far as we know, no direct measurement of the velocity of electric waves has been hitherto published. A number of experiments have been performed on the velocity of single pulses of electricity travelling over long metallic circuits, by Wheatstone, Fizeau and Gounelle, Siemens, Blondlot[†], and others; but the results obtained are very discordant. Blondlot's method is not open to the objections that have been raised against some of the others; for his electric pulses theoretically were short, and had steep wave fronts. Blondlot[‡] also described a method of determining the velocity of a system of electric waves. He measured the distance between the nodes on a metallic circuit, but, in order to get the time, he calculated the period of oscillation of another circuit that was in resonance with the first. His determination, therefore, was not a direct measurement.

Early last year the following direct method of measuring the velocity of electric waves suggested itself to us:—Increase the size, and if necessary change the shape of a Hertz vibrator until the period of oscillation is sufficiently long to be determined by photographing the spark; measure the length of the waves induced in a secondary circuit tuned to resonance with the vibrator; and the quotient of the wave-length by the time of a complete oscillation will be the required velocity.

The first apparatus experimented with was that used by Mr. St. John in investigating the peculiarities of waves along iron wires. For a detailed description of this apparatus see the Philosophical Magazine for November 1894. It has been assumed by certain writers that the reaction between the circuits, arranged in the manner employed by Mr. St. John, is, to a large extent, what would be called in the older theory of electricity electromagnetic rather than electrostatic. Certain phenomena, however, which appeared in the early part of our investigation seemed to point to the view that the greater portion of the action was electrostatic; and we therefore concluded to arrange the apparatus so that the reaction should be wholly electrostatic, thinking by this means to obtain a more powerful oscillation and a more regular wave than with the electromagnetic arrangement described and

[*] Communicated by the Authors.
[†] *Comptes Rendus*, 1891, tome xiii. p. 638.
[‡] *Ibid.* 1894, tome cxvii. p. 543.

used so successfully by Blondlot.   The first attempt arranged on the electrostatic principle proved a complete failure.   A second trial about a fortnight later, however, was so successful that we fully determined to adopt the electrostatic method.

The first point in the course of the investigation worth detailed description is the production of electric waves along parallel wires in such a manner that they are actually visible to the eye.   The arrangement of the apparatus to accomplish this was as follows :—

Fig. 1.

G   K

E

A   B   C   J

F

H   L
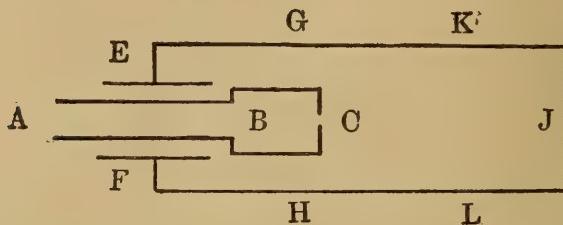
A primary condenser AB (fig. 1) was held with its plates in vertical planes by means of suitable wooden supports (not represented in the figure), and was joined in a circuit BC consisting of two wires about 75 centim. long placed 4 centim. apart.   In reality this circuit BC should be represented as perpendicular to the plane of the paper (which is taken as the horizontal plane passing through the centre of the apparatus). The plates of the condenser AB were sheets of tinfoil 101×40 centim. glued to hard-rubber sheets, and the dielectric between them consisted of other similar sheets of hard rubber sufficient in number and thickness to make the distance between the condenser plates $4 \cdot 2$ centim.   Outside the primary condenser plates and separated from them by hard-rubber plates (total thickness $\cdot 6$ centim.) were two secondary plates, E and F, each 40 centim. square.   To these plates was attached the secondary circuit EGJHF, the form of which is represented in the figure.   This latter circuit consisted of copper wire, diameter $\cdot 13$ centim., and its total length from E to F was 4200 centim.   A spark-gap with spherical terminals $2 \cdot 5$ centim. in diameter was placed at C in the primary circuit, and another spark-gap with pointed terminals was sometimes inserted at J in the secondary circuit, although this latter spark-gap had no effect upon the phenomena to be described.   The primary condenser was charged by means of a large Ruhmkorf coil excited by five storage-cells with a total voltage of ten volts.   The current from these cells was made and broken by the automatic interrupter used by Mr. St. John and described by him in his paper above referred to.

Every time the primary condenser was charged a spark passed at C, causing an oscillatory discharge. A convenient method of forming a mental picture of the oscillation excited in the secondary circuit is the conception of Faraday tubes elaborated by J. J. Thomson, in his 'Recent Researches in Electricity and Magnetism.' The oscillations of the primary acted inductively upon the secondary and sent out groups of Faraday tubes which travelled along the secondary circuit, with their ends on the wires, and lying chiefly in the space between them. At the end J they reversed their direction and travelled back along the circuit. The period of oscillation of the primary circuit was altered, until by trial it was found that groups of returning tubes met groups of advancing tubes between the points G and H. As the two sets of moving tubes were oppositely directed, they annulled each other and produced a node. Thus a system of stationary waves was set up with a node at J, another node at G H, and a ventral segment at K L. The method of discovering when the circuits were in tune and of investigating the shape of the waves will be described later. The point to be noticed here is that the vibrations were sufficiently powerful to cause a luminous discharge on the surface of the wire where the accumulation of tubes was a maximum, *i. e.* at K L, while at the nodal points J and GH the wire was entirely dark. Still further, the wave formation could be made apparent to the sense of hearing as well as that of sight ; for placing the ear within a few centimetres of the wire and walking beside it, a distinct crackling sound could be heard at the points K and L, whereas no such sound could be heard at G, J, and H. By placing bits of glass tubing on the wire the sound was much intensified at the points K and L, and the phenomena made more striking. It might be supposed that by decreasing the capacity of the primary condenser, and therefore the period of its oscillation, the secondary circuit could be broken up into a new set of shorter stationary waves, with nodes at J and at points somewhere near K, L, G, and H, and ventral segments between them. This we tried with perfect success, except that it was not possible to cause the light at K and L to actually disappear. There was decidedly less light at these points, however, than on either side of them. The light of course is simply that which always appears around wires carrying very high potential currents, the interesting point being that it appears in some places on the circuit and not in others. The experiment showing how the circuit breaks up in several different ways would form a most beautiful lecture experiment.

As a means of ascertaining when the circuits were in resonance, and of investigating the form of the wave in the secondary circuit, a bolometer similar to that designed by Paalzow and Rubens* was used.

The bolometer as an instrument for measuring electric waves is so well known, that it is not necessary to state here more than its fundamental principles. It consists essentially of a well-balanced Wheatstone bridge to one of the arms of which are metallically connected two small conductors. These conductors are brought near the circuit to be tested, and the oscillating charges induced in them and sent through the arm of the Wheatstone bridge develop enough heat to throw the bridge out of balance. By moving the conductors along the circuit different deflexions are produced according to the magnitude of the charges on the wire in their neighbourhood, and thus an excellent estimate of the wave formation can be obtained. In the present case the conductors that were brought near the secondary circuit consisted of two pieces of wire insulated with rubber, bent into circles of about 2 centim. radius, and fastened to a bit of pine-wood by means of a heavy coating of paraffin. The two wires of the secondary circuit passed through holes in this bit of wood in such a manner as to pass through the centres of the two circles. In the early part of the investigation the bolometer and galvanoscope were placed at a sufficient distance from the oscillating circuits to prevent any direct action of one on the other, and the leads running from the circular conductors to the bolometer consisted of long fine wires. Later, when longer circuits and longer waves were experimented with, great inconvenience was experienced from the long leads, since their relative position had considerable effect upon the galvanoscope deflexions. In order to obviate this difficulty short leads of heavily insulated wire were used, and the bolometer was placed on wheels and moved along from place to place. A bolometric study of the circuit just described showed the character of the oscillation to be that mentioned, namely, nodes at the points J, and GH, and a ventral segment at KL. A careful run was made from one end of the circuit to the other, which furnished data from which a very regular curve was drawn.

The insertion of a small spark-gap (1 millim.–3 millim.) at the point in the secondary circuit marked J (fig. 1) had no appreciable effect upon the position of the nodal point GH, or of the point of maximum accumulation KL. The form of

* Anwendung des bolometrischen Princips auf electrische Messungen," Wied. *Ann.* xxxvii. p. 529.

the wave was slightly altered for a metre on each side of J, and the bolometer showed a slight accumulation in the immediate neighbourhood of the spark-gap. This was probably due to the charging of the spark terminals to a sufficiently high potential to break through the dielectric. The fact that the insertion of a spark-gap into a secondary circuit in the manner described has no effect upon the length of the waves set up in that circuit was tested for a number of different cases (in none of which, however, was the length of the waves greater than in the present case), and found to be true in each one of them.

In order to determine the time of vibration we used a concave rotating mirror; and the images of the oscillating sparks were thrown on a sensitive plate. If the mirror rotated about a horizontal axis, the photographs showed bright horizontal lines, perpendicular to which at their extremities extended two series of dots. Fig. 2 is an enlargement (about ten times) of one of the sparks taken in our final measurement. The dots represent discharges from the negative terminals only, the positive discharges not being brilliant enough to affect the plate. The distance between successive dots was the distance on the plate through which the image of the spark-gap moved during the time of a complete oscillation. Hence by determining the speed of the mirror and measuring the distances from the mirror to the plate the time of oscillation could be calculated. To measure the sparks we used a sharp pointer moved at the end of a micrometer-screw under a magnifying-glass of low power. The instrument was originally intended for microscopic measurements, and was very accurately constructed. The rotating mirror was driven by an electric motor by means of a current from a storage-battery of extremely constant voltage. To give great steadiness a heavy fly-wheel was attached to the axis of the mirror. The speed of the mirror was determined to within about one part in five hundred by means of an electric chronograph. This apparatus, requiring great technical skill, was made for us by the mechanician of the laboratory. The mirror consisted of a thick piece of glass with a concave surface accurately ground for this research by the well-known optician Alvin Clark, and silvered by ourselves. For the extremely sensitive dry plates which were used we are indebted to Mr. Gustav Cramer, of St. Louis, Mo.

There are many advantages in photographing the secondary spark rather than the primary. In the first place, to properly photograph a spark it is necessary to use pointed terminals; but experiment has shown that the waves excited in a secondary

Fig. 2.
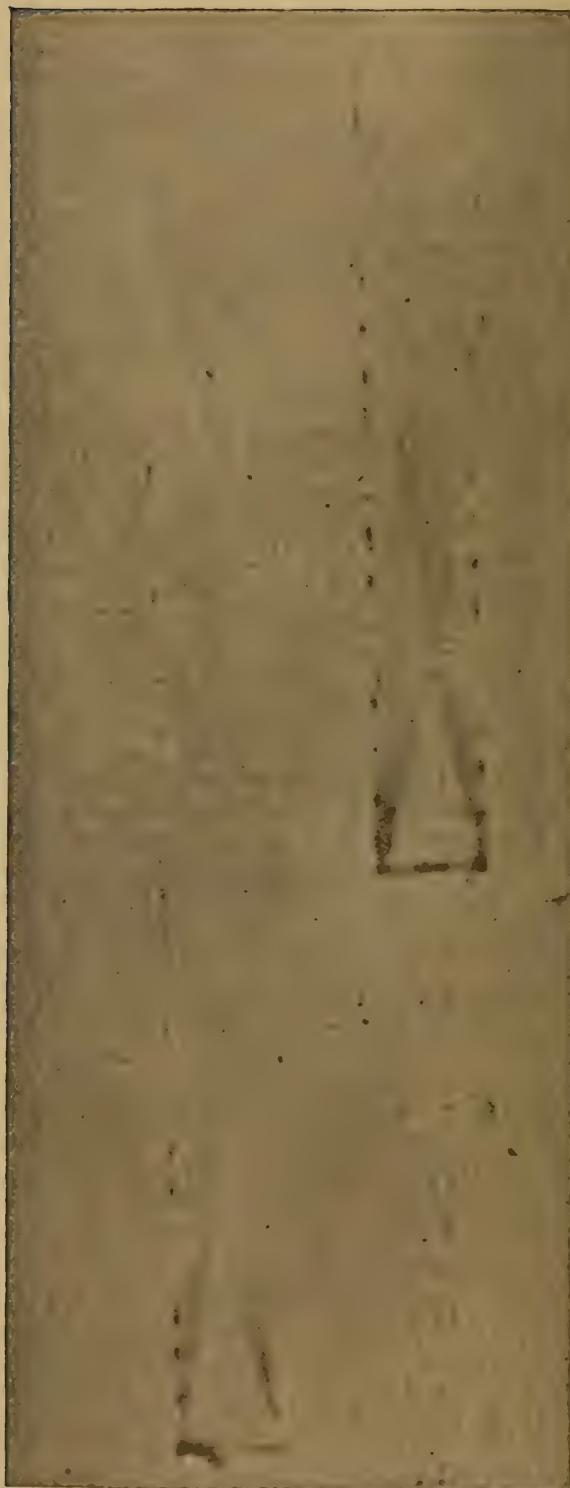
circuit depend to a large extent upon the character of the primary spark, and that the most active sparks are those between metallic spheres with polished surfaces. It is true that waves can be produced by sparks between points, but the oscillations are not so powerful or well marked. In the second place, from the results obtained by Bjerknes one would expect the oscillations in the secondary circuit to be much less damped than those in the primary. This expectation has been fully realized. Photographs show from ten to twelve times as many oscillations in the secondary as in the primary. The longest secondary spark we counted indicated 60 complete oscillations. In the third, and by no means the least important case, the question how close the resonance is does not affect the accuracy of the results. By photographing the sparks in the secondary the period of oscillation is determined, not of a circuit that is altered until by trial it is found to have as nearly as possible the same period of vibration as the circuit on which the length of the wave is measured, but that of the circuit along which the wave itself is actually travelling ; and hence the conclusions in regard to the effect of damping reached by Bjerknes in his admirable paper on "Electric Resonance"* do not affect the accuracy of the results.

The great difficulty to be overcome is the production of secondary oscillations that will produce sparks sufficiently bright to photograph. It is comparatively an easy task to photograph the primary spark, but in order to photograph the secondary the dimensions of the circuit must be chosen with great care.

With a view to increasing the light of the spark, together with the length of the waves, it seemed desirable to lengthen the period of oscillation by enlarging the condensers rather than by increasing the self-induction of the primary circuit. A castor-oil condenser therefore was designed and constructed on the following plan :—Eight plates (25 centim. × 20 centim.) were cut out of sheet zinc, and were held in vertical planes side by side 2 centim. apart by a suitable hard-rubber frame. The plates were entirely immersed in castor-oil contained in a glass jar. They were connected together in the manner shown in fig. 3. The plates marked a, c, and e were fastened to the conductor A B, and formed one armature of the condenser. Those marked d, f, and h were joined to C D and formed the other armature. The two ends of the secondary circuit E, G, J, H, F were fastened to the plates b and g. The plane of the secondary circuit was 50 centim. and that of the primary 3 centim. above the upper edge of the condenser

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* "Ueber electrische Resonanz," Wied. *Ann.* lv. p. 121 (1895).

plate.   The total length of the secondary circuit from one condenser plate through E, G, J, H, F to the other plate was 6338 centim.   The circuit consisted of copper wire (diameter ·215 centim.) supported at each end by suitable wooden frames, and also once in the middle by hard-rubber hooks, fastened by long pieces of twine to a wooden crossbar above.   The distances from F to E and from K to L were 30 centim., and a spark-gap with pointed tin terminals was inserted at J.   The primary circuit consisted of copper wire (diameter ·34 centim.). The distances between the two parts A B and C D were 45 centim.   The portion B D contained a spark-gap with platinum-faced spherical terminals, and was made so as to slide back and forth, to and from the condenser.   The motion of this movable piece varied the self-induction, and therefore the period of oscillation of the primary circuit.   By this

Fig. 3.
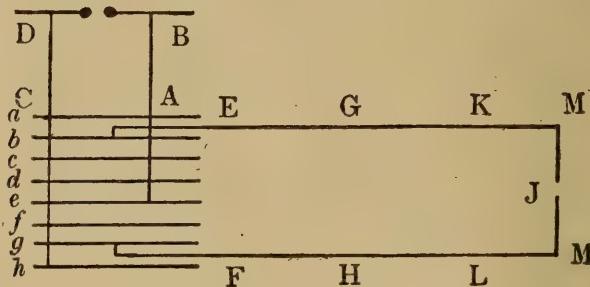
means the circuits were brought into resonance.   With certain arrangements of the condensers the resonance was very sharp, and the position of the movable portion could be determined to within ·25 centim.   In the arrangement which was finally adopted the resonance was not so sharp.   Even in this case the distance of the sliding part from the plate *a* could not have been in error by more than 2 centim.   The length 65 centim. was finally chosen for its value.

The automatic current-interrupter that worked so beautifully in connexion with the Hertz vibrator would not function well when used to excite the circuits just described.   After trying many devices, we finally adopted an ordinary reed interrupter with a comparatively large hammer-and-anvil arrangement, which gave little trouble.

At first it was found impossible to produce anything but a complex vibration in the secondary circuit when the spark-gap was open.   Some slight evidence of resonance was obtained, but nothing of a decided character.   When, however, the spark-gap was closed, very good resonance ensued, and a wave the length of which could be measured to within ·4 per cent. was excited.   Some photographs were taken of

the spark in the secondary circuit, and they showed immediately the character of the complex wave-formation. The secondary circuit could and did oscillate in three different ways, and the ratios of the periods were those of the notes in an open organ-pipe, namely 1:2:3. Usually the lowest or fundamental oscillation together with one of the overtones was present ; but several sparks were noticed that furnished unmistakable evidence of the simultaneous existence of all three. We have observed in a circuit 10,000 centim. long the same peculiarities of oscillation, excited by a primary circuit that, judging from its dimensions, could not have been in resonance with the secondary. It was evident that the oscillation having a node between the points marked E and F (fig. 3) is that whose period is one third of the fundamental.

A number of measurements of this period have been made, and from these values the velocity of the waves has been calculated. The results appear in the following table. As an average of five measurements of the wave-length, none of which differed from the mean by more than 20 centim., the value 5888 centim. was chosen. The distance from the mirror to the photographic plate in each case except the last was 300·1 centim. Each of the first five values in the second column of the table is an average of thirty measurements of distances ranging in the neighbourhood of 1 centim.

Number of Revolutions of Mirror per second.	Distance between two successive points on Plate, centim.	Velocity of Waves, centim.
71·2	·05608	$2·819 \times 10^{10}$
70·85	·05600	$2·810 \times 10^{10}$
70·7	·05532	$2·835 \times 10^{10}$
71·3	·05637	$2·808 \times 10^{10}$
70·8	·05611	$2·808 \times 10^{10}$
	Average ...	$2·816 \times 10^{10}$
69·2	·05340	$2·988 \times 10^{10}$

The last line in the table contains the results of measurements on photographs of the primary spark instead of the secondary. In this case the distance from the mirror to the photographic plate was 311·5 centim.

These results we published as a preliminary record in the American Journal of Science for April 1895. At that time we did not think, judging from the table as it stood, and from a consideration of the possible errors in the various measurements, that the total error in our determination could have been as great as the difference between the average just

quoted and $2 \cdot 998 \times 10^{10}$, which is generally accepted as the velocity of light. Since then we have succeeded in producing much better waves and much more regular sparks, and have discovered a phenomenon which renders a measurement on a photograph over a space where the dots are obliterated a questionable proceeding. The new data have given a value for the velocity more in accord with theory.

Since the waves in the secondary were not well formed when the spark-gap was inserted, it seemed desirable to try to find an arrangement that would produce simultaneously a good wave and a photographable spark. A number of condensers with plates of different sizes and shapes and different substances for the dielectric were tried, and the apparatus to be described was finally adopted. The difficulties to be overcome were these. Too strong a reaction between the primary and secondary condensers could not be employed, because the increase in the damping of the primary due to the large amount of energy drawn off by the secondary made good resonance impossible. The amount of energy in the primary at full charge must be much greater than that in the secondary. On the other hand the capacity of the primary condenser must not be too great; for the self-induction of the primary circuit would have to be proportionately small, and this, too, means an increase in the damping. The secondary condenser, too, must have a capacity of less than a certain magnitude in order that the node may fall on the circuit and not in the condenser plate. These points seem to indicate that small condensers are preferable to large ones; but a decrease in the size of the plates means a decrease in the light of the secondary sparks, and the sparks are at best barely photographable. Practically, therefore, our choice was much limited, and the particular arrangement to give the best results had to be selected by experiment after a long series of trials. The arrangement and dimensions of the apparatus finally adopted were as follows :—

Two metallic plates, *a* and *b* (fig. 4), 30×30 centim., placed

Fig. 4.
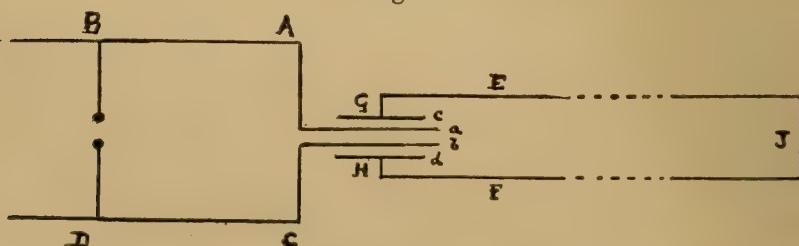
in vertical planes, formed the primary condenser. The dielectric between them consisted of the best French plate-glass obtainable ($K = 8 +$ probably) and was 2 centim. thick.

Outside the plates *a* and *b*, and separated from them by a hard-rubber dielectric (K = 2 + about) 1·8 centim. thick, were the secondary plates, 26 × 26 centim. The primary and secondary circuits were joined to the condenser plates as indicated in the figure. The primary circuit lay in the horizontal plane passing through the centres of condenser plates, and consisted of copper wires ·34 centim. in diameter. In order to control the period of oscillation of the primary circuit, the portion B D containing a spark-gap with spherical terminals was made, as before, so as to slide along parallel to itself. The distance between the straight portions A B and C D was 40 centim., and the lengths of A B and C D finally chosen for best resonance were 85 centim. Most of the secondary circuit lay in a horizontal plane 16 centim. above that of the primary. The lengths G E and H F, however, were bent down and fastened to the middle points G and H of the secondary plates. The circuit consisted of copper wire (diameter ·215 centim.), and its total length from G through J to H was 5860 centim. At J was a spark-gap with pointed terminals. With this apparatus we succeeded in producing a very regular wave-formation, as indicated by the bolometer, even when there was a spark-gap at J. So many curves have been plotted and published to illustrate the characteristics of electrical waves that it does not seem worth while to add to the number here. It will be sufficient to state that the ratio of the maximum and minimum deflexions in the bolometer was about 15 : 1, and that there was a node at J, and another about 40 centim. to the right of E and F.

Upon photographing the secondary spark some curious phenomena were observed. In the first place the dots usually appeared in pairs. There would be two black dots followed by a space where two or three dots either appeared faintly or were absent altogether, after that the two black dots would reappear followed again by a faint space, and so on for six or seven repetitions. All this of course occurred in a single spark.

The explanation that first presents itself is that the two black dots are the result of the first two oscillations in the primary circuit, which, owing to the damping, are much more powerful than the others. If this were the true reason the first of the pair of dots always ought to be blacker than the second, and every third dot ought to be the first of a pair. This is not the case, however. On the other hand, the phenomena cannot be explained as the result of a complex vibration ; for the bolometer-readings, taken only a few minutes before the photographic plates were exposed and with exactly the same arrangement of apparatus, indicated extremely regular waves. A clue to the mystery was furnished

by several sparks in which the dots made by one spark-terminal had the characteristics just described, whereas those made by the other were quite regular. Following out this hint, we found that the particular substances used for the secondary spark-terminals had a large effect upon the characteristics of the photographs. We tried spark-terminals made of a number of different metals—tin, aluminium, magnesium, fuse-metal, &c., and finally adopted cadmium as productive of the best sparks. In the case of cadmium the characteristics described are much less marked, and we have succeeded even in producing a few sparks in which no difference in blackness could be detected between one dot and the next. The photographs from cadmium terminals, too, are far more distinct and far more easily measured than those from terminals of any other metal that we tried.

An interesting question arose here as to whether the distance between two successive dots would depend upon the period of oscillation of the primary circuit if the secondary were unaltered. To test this point the circuits were brought into resonance and a photograph taken. The self-induction of the primary circuit was increased by about 20 per cent. of its value and a second photograph taken. In the first case the distances between successive dots were all within 2 or 3 per cent. of the average obtained by measuring over several dots and dividing by the number of intervening spaces ; whereas in the second case the measurements of some of the single spaces were from 8 to 12 per cent. greater than before, the average from long measurements being the same. This indicates that the vibrations of the secondary circuit are not necessarily perfectly regular, and at a distance apart fixed by the character of the circuit, but are to be looked upon as a series of pulses started travelling along the circuit and keeping at a distance from each other that is determined by the exciter. Owing to the fact that the damping of the primary is much greater than that of the secondary, the seventh and eighth pulses started are too weak to obliterate the first and second which have travelled the length of the circuit and back. We should expect from this that the bolometer throws, which measure the average length of the wave, would not indicate a shifting of the node when the circuits are thrown slightly out of resonance, but that the minimum throws would be greater than when the circuits are exactly in resonance. This, as is well known, is what happens.

The improved sparks which the new arrangement of apparatus and the use of cadmium as material for the spark-terminals have enabled us to produce, have brought to light another interesting fact, namely that, even when the best

resonance is obtained and the most regular wave-formation is excited, the distances between the first three or four dots are slightly greater than the distances between three or four dots taken farther down the spark. The explanation we offer for this is the following, and it applies as a criticism to all cases in which waves are excited in a circuit by a neighbouring circuit possessing a much larger damping factor. The fact that the secondary waves last longer than the primary oscillations means that the last times that the waves travel over the circuit they do so under different end conditions from the first few times. The capacity of the secondary plates is slightly less after the primary spark has stopped than it was before, and therefore the length of the wires equivalent to the secondary plates is slightly less, and it takes a shorter time for the waves to travel along the circuit and back. Hence the observed decrease in the distance between the spark-points and a certain mixing up of the dots, which occurs after the sixth or seventh oscillation (see fig. 2). The sixth dot in the figure, apparently following its predecessor after about half an interval, is not a usual characteristic. In the vast majority of sparks the first few dots are far more powerful than those that follow them, and only occasionally do sparks occur that indicate more than five or six good complete oscillations. Hence these first few oscillations have the preponderating influence in fixing the length of the waves as indicated by the bolometer. In examining the sparks, therefore, we measured from the first oscillation as far down the spark as we could without passing over a space where dots were obliterated ; and hence in every case we knew the number of dots between the points from which measurements were taken, and did not have to assume that good oscillations had occurred without affecting the plate.

The following table, containing the results of our measurements with the improved apparatus, explains itself. The distance from the mirror to the photographic plate was 302 centim. in each case :—

Number of Revolutions of Mirror per sec.	Distance between successive points on Plate, centim.	Time of Oscillation, seconds.	Length of Wave, centim.	Velocity of Wave, centim. per sec.
70·8	·05028	$1·871 \times 10^7$	5670	$3·030 \times 10^{10}$
73·7	·05247	$1·876 \times 10^7$	5670	$3·022 \times 10^{10}$
75·2	·05536	$1·940 \times 10^7$	5670	$2·923 \times 10^{10}$
69·5	·05002	$1·897 \times 10^7$	5690	$3·000 \times 10^{10}$
68·9	·04900	$1·874 \times 10^7$	5690	$3·036 \times 10^{10}$
69·0	·04974	$1·899 \times 10^7$	5690	$2·996 \times 10^{10}$
71·2	·05075	$1·878 \times 10^7$	5660	$3·014 \times 10^{10}$
Average Value of Velocity				$3·003 \times 10^{10}$

With the exception of three preliminary trials, which gave values differing from the mean by 10 per cent. or by 12 per cent., these are the only determinations we have made. In some cases the waves in the circuit were just as good with the spark-gap as without it. In others there was a decided wave-formation when sparks occurred, but the node was not quite so well-marked. For this reason, and since it did not appear to make any difference in their length, the waves usually were measured without the spark-gap. As the sparks were quite regular, the difference in the bolometer readings must have been due to Faraday tubes that were reflected from the spark-gap without forming a spark and reversing themselves. The variation in the number of revolutions of the mirror per second is due to the fact that different cells were used to drive the motor on different occasions.

As an example of the data taken to ascertain the position of the node we give the following table. The top line contains the distances of the bolometer terminals from a pair of arbitrary fixed points on the circuit :—

Distances from fixed points	20 cm.	40 cm.	60 cm.
Bolometer deflexions	$\begin{cases} 4\cdot3 \\ 4\cdot5 \\ 4\cdot5 \end{cases}$	$\begin{matrix} 4\cdot0 \\ 4\cdot1 \\ 4\cdot0 \end{matrix}$	$\begin{matrix} 4\cdot3 \\ 4\cdot4 \\ 4\cdot2 \end{matrix}$
Average deflexions	4·43	4·03	4·3

From these deflexions the position of the node was estimated. It appears from the best results that we have obtained, that the velocity of short electric waves travelling along two parallel wires differs from the velocity of light by less than ·2 per cent. of its value. It has been shown theoretically, that the velocity of such waves travelling along a single wire should be the velocity of light approximately. Our results, therefore, in a certain sense confirm the theory to an accuracy within their probable error. Theoretically, too, the velocity should be approximately equal to the ratio between the two systems of electrical units. The average of the best measurements of this ratio is 3·001, which is nearer the average velocity obtained by us than the velocity of light.

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XVI. *Fractional Distillation applied to American Petroleum and Russian Kerosene.* By J. Alfred Wanklyn *and* W. J. Cooper[*].

WE entertain a higher opinion of the possibilities of Fractional Distillation than is admitted by the great majority of chemists. According to our view separations are possible where there is any difference of volatility : and we hold that, unless chemical action of some description frustrates the separating process, there is no limit to the possibility of separation and purification by fractional distillation in all cases where the components of the mixture differ in *volatility*. By the word volatility we do not mean quite the same thing as vapour-tension. The relative volatility of two liquids (as one of us pointed out more than thirty years ago in a paper in the Proceedings of the Royal Society) is expressed not by the vapour-tension, but by vapour-tension multiplied by vapour-density. There must be instances, but they are very rare, where two liquids of different vapour-tensions have identical volatility. Putting such cases on one side, we hold that, unless chemical action bars the way, there is no limit to purification by fractional distillation.

Our method of working differs, vitally we are disposed to think, from the ordinary manner in which chemists carry out the process of fractionation. Our process is exhaustive : hitherto the method in common use has not proved to be exhaustive, but has missed out many terms of the series to which it has been applied.

In our paper published in May 1894, in the Philosophical Magazine, we gave an account of our work on Russian Kerosene, showing a series of hydrocarbons rising in the scale, not by increments of 14 but by increments of 7.

We have applied our exhaustive fractionation to the American Petroleum of commerce, and, so far as we have investigated, a precisely similar state of things is found in the American liquid as in the Russian. Restricting ourselves at first to the more volatile portion of the oil, we find an homologous series with the common increment of 7 instead of 14. The admirable research of Cahours and Pelouze, which dates back to the years 1862 and 1863, established that these American hydrocarbons belong to the Marsh-gas family. We have now come across the same hydrocarbons, and we have found other hydrocarbons which fractionation, as practised in the years 1862 and 1863, had missed.

In our hands fractional distillation furnishes liquids which

[*] Communicated by the Authors.

are not correctly described as being *fractions,* but are properly termed the *fractionation-products.*

The American Petroleum upon which we have operated is a most abundant commercial article. We found the sp. gr. at 18° C. to be 0·7924. Tested with slightly diluted sulphuric acid it did not diminish in volume. A preliminary experiment in the retort showed that its distillation covered a great range of temperature. Thus, in operating upon a charge of 600 cubic centim. and distilling into graduated measuring-glasses, we made the following readings of thermometer and distillate :—

At 157° distillation began.
Up to 170° distillate measured   50 cubic centim.
,,   184°   ,,   ,,   100   ,,   ,,
,,   196°   ,,   ,,   150   ,,   ,,
,,   209°   ,,   ,,   200   ,,   ,,
,,   227°   ,,   ,,   250   ,,   ,,
,,   247°   ,,   ,,   300   ,,   ,,
,,   264°   ,,   ,,   350   ,,   ,,
,,   270°   ,,   ,,   360   ,,   ,,
          Residue in retort = 240   ,,   ,,

The original liquid upon which we have carried out this investigation was in this manner shown to be of such a nature as to rise 90 degrees Centigrade in yielding half of its volume of distillate, and to yield nothing at all below 157° C.

Our actual operation was carried out on a considerable scale, and our fractionation-products are as follows :—

There is first of all a small proportion of very volatile liquid, the fractionation of which we have not yet attempted, but which we expect to fractionate on a future occasion. This most volatile lot amounts to about one per cent. of the original petroleum. Then we have seven fractionation-products, amounting on an average to 3·06 per cent. of the original petroleum. Each of these seven fractionation-products is a single chemical substance of sufficient purity for proper identification. As we have mentioned, these substances obtainable from American petroleum were shown by Cahours and Pelouze to be members of the same family as Marsh-gas. Adopting 6 as the atomic weight of carbon, the formula of Marsh-gas becomes C_2H_4 ; and taking $CH = 7$ as the common increment of the series, we have C_2H_4 ; C_3H_5 ; C_4H_6 as the second, third, and fourth terms.

Our seven hydrocarbons extracted from American petroleum have the following formulæ :—

$C_{15}H_{17}$; $C_{16}H_{18}$; $C_{17}H_{19}$; $C_{18}H_{20}$; $C_{19}H_{21}$; $C_{20}H_{22}$; and $C_{21}H_{23}$.

We propose to name the members of the series as follows:—

$C_{15}H_{17}$, Marsh xv. ; $C_{16}H_{18}$, Marsh xvi. &c.

Tabulating our results we arrive at the following :—

	Vapour-Density.		Sp. Gr. at 15°·5C.	Boils at ° Cent.	Percentage of Hydrocarbon in Acetic Compounds.	
	Theory.	Found.			Theory.	Found.
Marsh xv.	3·697	3·611	0·7202	95	.	
„ xvi.......	3·939	3·977	0·7305	107		
„ xvii. ...	4·181	4·165	0·7355	119	66·85	66·62
„ xviii. ...	4·422	4·377	0·7468	130	6ọ·09	68·15
„ xix.......	4·664	4·624	0·7521	141	69·23	69·18†
„ xx.	4·906	4·908	0·7579	152	70·30	70·05
„ xxi.......	5·148	5·148	0·7633	160	71·29	71·68

† Mean.

The vapour-densities were determined by the Dumas method, corrections for expansion of the glass globe being made and great care taken to ensure accuracy. As will be seen, the agreement between the theory and the values actually found is quite close enough.

Some of the fatty acids, viz. Acetic Acid, Butyric Acid, and Valerianic Acid, have been shown to enter into chemical combination with these hydrocarbons. In the Table the percentage of hydrocarbon found in such compounds is given.

Our investigation of Russian Kerosene has furnished the following results :—

		Vapour-Density.		Sp. Gr. at 15°·5 C.	Boils at	Percentage of Hydrocarbon in Acetic K.	
		Theory.	Found.			Theory.	Found.
Ay	xiii.	3 144	3·192	0·7350			
Az	xiv.	3·386	3·43	·7460	85	62·04	62·33
Aa	xv.	3·63	3·69	·7510	96·5	63·63	62·75
Ab	xvi.	3·87	3·91	·7576	106	65·12	64·48
B	xvii.	4·11	4·08	·7606	116·5	66·48	65·9†
Bb	xviii.	4·35	4·36	·7711	127	67·74	67 84
Bc	xix.	4·59	4·59	·7768	138	68·91	69·06
C	xx.	4·84	4·84	·7843	148	70·00	69·70
D	xxi.	5·08	5·02	·7975	158	71·01	70·94
Dd	xxii.	5·32	5·20	·8057	168	71·96	72·00†
De	xxiii.	5·56	5·51	·8090	176	72·87	72·99
E	xxiv.	5·80	5·77	·8185	186	73·68	74·01
F	xxv.	6·04	6·08	·8240	197	74·47	74·64
Fg	xxvi.	6·28		·8255	205	75·21	75·28
G	xxvii.	6·52	6·53	·8270	214	75·90	77·02
Gg	xxviii.	6·77	6·82	·8287	222	76·56	77·31
H	xxix.			·8338	230	77·18	77·53
Hh	xxx.			·8392	237	77·77	77·53
I.........	xxxi.			·8430	246	78·34	78·34†
K	xxxii.			·8470	253	78·87	79·43
L	xxxiii.			·8520	260	79·38	79·95
M	xxxiv.			·8560	267	79·87	79·83
N	xxxv.			·8590	274	80·33	80·63†
O	xxxvi.			·8603	280	80·77	80·55

† Mean.

We would call attention to the regular parallelism between the American Marsh hydrocarbons and the Russian Kerose hydrocarbons.

Number of small carbon atoms in the hydrocarbon.	Russian.		American.	
	Sp. Gr. at 15°·5.	Boiling-point.	Sp. Gr. at 15°·5.	Boiling-point.
xv.	0·7510	96·5	0·7202	95
xvi.	0·7576	106	0·7305	107
xvii.	0·7606	116·5	0·7355	119
xviii.	0·7711	127	0·7468	130
xix.	0·7768	138	0·7521	141
xx.	0·7843	148	0·7579	152
xxi.	0·7975	158	0·7633	160

Showing that the same carbon-condensation in the hydrocarbon gives a slightly heavier liquid in the Russian series. The difference in specific gravity being as follows :—

xv. . . . . . . ·0308
xvi. . . . . . . ·0271
xvii. . . . . . . ·0251
xviii. . . . . . . ·0243
xix. . . . . . . ·0247
xx. . . . . . . ·0264
xxi. . . . . . . ·0342

Showing a small but not always exactly the same increment of specific gravity in the case of the Russian hydrocarbon as compared with the American.

XVII. *Proceedings of Learned Societies.*

GEOLOGICAL SOCIETY.

[Continued from p. 152.]

March 6th, 1895.—Dr. Henry Woodward, F.R.S., President, in the Chair.

THE following communications were read :—
1. 'A new Ossiferous Fissure in Creswell Crags.' By W. L. H. Duckworth, Esq., and F. E. Swainson, Esq.

2. 'Notes on the Chemical Composition of some Oceanic Deposits.'
By Prof. J. B. Harrison, M.A., F.G.S., and A. J. Jukes-Browne,
Esq., B.A., F.G.S.

The authors formerly experienced great difficulty in comparing
their analyses of the Oceanic Deposits of Barbados with those of
modern oozes made by Dr. Brazier. Since then Dr. Murray has
placed samples of recent Red Clay and *Globigerina*-ooze at their
disposal, and these were analysed by Prof. Harrison and Mr. John
Williams.

The results of analysis of the Red Clay were arranged as follows :—
Argillaceous constituent 67·85 per cent., pumiceous matter 23·26
per cent., organic constituents 5·88, and adherent sea-salts 3·61
per cent. The authors found that the argillaceous constituent was
not a mixture of an orthosilicate of alumina and hydrated peroxide
of iron, having the proportion of silica to alumina as 14 to 12,
but a more highly silicated compound in which the proportions
were as 33 to 12. It was in fact a ferruginous earth, such as would
result from the decomposition of palagonite and of a basic volcanic
glass, fragments of which were frequent in the Pacific red clays.
The pumiceous matter was the débris of an acid pumice containing
7 per cent. of soda, and apparently therefore the pumice of a soda-
felsite. Comparing the analyses of the recent Red Clay with those of
Barbadian red clays, they find the differences to be such as would
result from mixtures of the palagonitic earth with various acid and
basic pumices. A mixture of the palagonitic earth with the
pumiceous dust which fell on Barbados in 1812 would have a
composition closely corresponding to that of the Oceanic Clay of
Barbados.

The recent calcareous ooze closely resembled the more calcareous
'chalks' of the Barbadian Oceanic Series, but the latter contained
much colloid silica and fine clay. The differences between the
analyses of the recent ooze and of English chalk, when certain
allowances are made, were found to be but small. The recent
calcareous ooze contained many more *Globigerina*-tests than Tertiary
or Mesozoic chalks, but it is suggested that this is due to our
possessing only the surface-layers of the *Globigerina*-ooze.

In one important respect all the different kinds of deposit which
were examined resembled one another, namely, in the infinitesimally
small quantity of quartz which they contained.

The authors' examination of the recent oceanic deposits, and
a comparison of them with the raised Barbadian deposits, only
increased their conviction that the latter were of truly oceanic
origin.

March 20th.—Dr. Henry Woodward, F.R.S., President,
in the Chair.

The following communications were read :—

1. 'On Fluvio-Glacial and Interglacial Deposits in Switzerland.'
By C. S. Du Riche Preller, M.A., Ph.D., F.G.S., F.C.S., A.M.I.C.E.,
M.I.E.E.

This paper is the outcome of one published in the 'Geological

Magazine' of January 1894, on the 'Three Glaciations in Switzerland,' in which the author described various glacial deposits near the lake of Zürich. He now describes a series of fluvio-glacial conglomerates and interglacial lignite-deposits near the lakes of Zürich, Constance, Zug, and Thun, which, together with analogous deposits at the base of the Eastern, Western, and Southern Alps, constitute further evidence of two interglacial periods, and therefore of three general glaciations, the oldest of these being of Upper Pliocene, and the others of Middle and Upper Pleistocene age respectively. As regards the origin, age, and the time required for the formation of several of the Swiss deposits referred to in the paper, the author arrives in several respects at conclusions differing from those recently enunciated by others. The author also argues that the first interglacial period was probably of shorter duration than the second; and in confirming his former conclusion that every general glaciation marks a period of filling-up, and every interglacial period marks a period of erosion of valleys, he avers that, if this conclusion be correct, it must needs be destructive of the theory of glacial erosion.

2. 'The Bajocian of the Mid-Cotteswolds.' By S. S. Buckman, Esq., F.G.S.

The Mid-Cotteswolds is defined as the district between the valleys of the Frome and the Chelt. A description of twenty-five sections is given, dealing principally with the strata found between the Upper *Trigonia*-grit and the Upper Freestone—such strata being called, for the purpose of present distinction, 'the intervening beds.' Of these twenty-five sections, seventeen, lying between Stroud and Leckhampton, are discussed in Part I. of the paper to show the succession of the intervening beds, to point out that Cotteswold geologists have confounded two distinct deposits, the Lower *Trigonia*- and Gryphite-grits, to prove that the former, and not the latter, is the more persistent stratum, and to give evidence that denudation, called 'Bajocian denudation,' has, prior to the deposition of the Upper *Trigonia*-grit, cut right through the intervening beds in the neighbourhood of Birdlip, so as to make a shelving trough 6 miles wide and about 30 feet deep.

The remaining eight sections are described in Part II. of the paper. They lie eastwards of Leckhampton, and are given to show the discovery of another ammonitiferous horizon in the Cotteswolds, yielding angustumbilicate *Witchelliæ*. It is proved that this bed is above the Notgrove Freestone and below the Upper *Trigonia*-grit; so that it is really an addition to the stratigraphical sequence hitherto recognized in the Cotteswolds. Its ammonites show it to have been deposited contemporaneously with the middle of the Sandford Lane Fossil Bed, and yet it is removed by 10 to 12 feet from the Gryphite-grit=lower part of that bed. In the Mid-Cotteswolds this important *Witchellia*-bearing bed is only preserved over an area of about $1\frac{1}{2}$ square miles, because it has been mainly removed by Bajocian denudation; and only one side of one small quarry yields

a favourable exposure. No other locality showing this deposit has yet been found in the county.

Two plotted diagrams are given to show the developments of the beds in the different sections, and to illustrate the result of the Bajocian denudation. In an Appendix to Parts I. and II. various notes are given, and attention is called to a remarkable oyster as a document of historic value evidencing the Bajocian denudation.

Part III. of the paper gives the chronological sequence of brachiopoda in Dorset and the Cotteswolds in the Inferior Oolite, to show their value for purposes of exact correlation when ammonites are absent; and to illustrate that the brachiopods are a good medium of exchange in regard to the strata of the Cotteswold and Dorset districts respectively, that in some cases they are such in regard to the two districts, and in other cases they fail in this respect, so that ammonites become the only true medium of exchange between the beds of different basins.

An Appendix to Part III. describes certain new species of brachiopoda, and gives notes upon others.

XVIII. *Intelligence and Miscellaneous Articles.*

ON THE MAGNETISM OF ASBESTOS. BY L. BLEEKRODE.

IN the 'Electrical Review' Mr. A. S. C. Swinton[*] states that asbestos is rather strongly magnetic. As this fact must be taken into account in constructing certain measuring instruments, I have repeated the experiments in question, and have found that in the material at my disposal[†] the magnetic force is even more strongly developed than Swinton mentions, in so far that powerful electromagnets were not necessary, but an ordinary good steel magnet was sufficient for demonstrating it. It is surprising that this property, which asbestos possesses in a higher degree than most magnetic substances (with the exception of nickel and cobalt), should have been so long overlooked, notwithstanding that this material has been so much in use, especially in late years.

Faraday, in his well-known investigations on the magnetic behaviour of various substances, places asbestos among the *feebly* magnetic bodies, which is remarkable, as he was working with a very strong electromagnet. Long before that, in the year 1778, my countryman Brugmans[‡], who discovered the diamagnetism of bismuth, in his researches on the magnetism of various bodies mentions asbestos as a tolerably strong magnetic mineral. He states that the steel magnet which was used in the experiments

[*] Electrical Review, vol. xxxiv. Oct. 5, 1894.
[†] From Bell's Asbestos Company.
[‡] 'Magnetismus seu de affinitatis magneticis observationes,' translated into German by G. Eschonbach : Leipzig, 1781, p. 138.

could hold about three pounds at each pole, and that the material investigated was moved easily on the surface of mercury. He also observed that the various kinds of asbestos are not magnetic to the same extent. He distinguishes "ripe" asbestos, consisting of short fibres in the same direction and of a straw colour; this is strongly magnetic and hangs to the poles. Another kind which he describes as "unripe," of greater tenacity and prismatic shape, is feebly magnetic.

I used a steel magnet which could support 3 kilos at both poles together, and found that a variety of asbestos of greenish colour and firm texture was only very slightly attracted when it was brought in a movable position opposite the poles of the magnet. On the other hand, asbestos cloth woven without any filling, of a grey kind, was attracted to both poles and held there like a thin iron wire. This was still more remarkably seen in a thin strip of what is known as asbestos-paper, about 4 centim. long and 0·3 centim. in breadth. This jumped from a distance of 1 centim. towards the poles of an electromagnet with a lifting force of 5 kilo. This strip showed afterwards (as Brugmans had already proved) slight polarity; I noticed at least that the pole of a magnetic needle was afterwards unequally attracted by the ends of the strip. With an electromagnet of about 100 kilos lifting-power the strip could also distinctly attract fine iron powder at the end turned away from the pole.

A square piece of asbestos paper, 15 centim. in the side, moved from a small distance towards the poles, and remained there even against a slight counterpoise. Of course small fibres of asbestos and splinters acted like fine iron turnings, and even from a distance of 8 centim. came in contact with the poles. Most preparations of asbestos for technical purposes are made with a packing the composition of which I do not know. I think, however, that even if iron should be among the constituents it would be in chemical combination with other elements as it is in the mineral itself, and, accordingly, could not be considered as the cause of the remarkably strong magnetism; there are evidently several iron compounds which show no attraction, and, as has been already observed, a preparation without filling was also strongly magnetic*.

In any case the observations of Swinton must not be disregarded in practice, since the use of plates of asbestos may give rise to sources of error in sensitive magnetic instruments.—Wiedemann's *Annalen*, June 1895.

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* I boiled some grey asbestos, which showed itself strongly magnetic, for a few hours with concentrated sulphuric acid; it had become quite white and had retained the magnetic property.

XIX. *The Electrical Properties of Selenium.*
By SHELFORD BIDWELL, *M.A., F.R.S.**

§ 1. *Preliminary* †.

SELENIUM, which is supposed to be an elementary substance, is capable of existing in several distinct modifications. The amorphous variety consists either of a finely divided red powder, or of a vitreous mass which resembles black glass in appearance and does not conduct electricity. Amorphous selenium melts at about 100° C, but at temperatures between 100° and 217° the black semi-liquid mass gradually hardens into a grey metallic-looking solid. This consists of Se in the crystalline form: it melts at 217°, and is a moderate conductor of electricity, its conductivity being temporarily increased by the action of light. This peculiar influence of light upon Se has attracted much attention, and below is given a list of published papers relating to the subject ‡.

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* Communicated by the Physical Society: read June 28, 1895.

† A summary of the principal results will be found at the end of the paper.

‡ Willoughby Smith, Journ. Soc. Tel. Eng. ii. p. 31; Earl of Rosse, Phil. Mag. March 1874, p. 161; Sale, Proc. Roy. Soc. 1873, p. 283; Phil. Mag. March 1874; Werner Siemens, Phil. Mag. November 1875, p. 416; Draper and Moss, 'Chemical News,' xxxiii. p. 1; Moss, Proc. Roy. Soc. May 11, 1876; Adams and Day, Proc. Roy. Soc. 1876, p. 113; Phil. Trans. 1877, p. 313; C. W. Siemens, Proc. Roy. Inst. 1876, p. 68; Sabine, Phil. Mag. June 1878, p. 401; Graham Bell, 'Nature,' xxii. p. 500; Proc. Nat. Acad. Sci. April 1881; Shelford Bidwell, Phil. Mag. April 1881, January 1883, August 1885, March 1891; Fritts, 'Electrical Review,' March 7, 1885, p. 208; Minchin, Phil. Mag. March 1891, p. 207.

§ 2. *Selenium Cells.*

Any device consisting essentially of a mass of crystalline selenium in combination with two metallic electrodes, and so arranged as to expose a relatively large surface for light to act upon is commonly, but not very appropriately, termed a "Selenium Cell." So many inquiries have reached me as to the construction of the sensitive cells which I have at different times exhibited before this Society and elsewhere, that I venture to think a short account of the process may be usefully given here.

A slip of mica about 55 millim. long, 17 millim. wide, and 0·4 millim. thick, is sandwiched between two semi-cylinders of boxwood about 18 millim. in diameter and of somewhat greater length than the mica, the ends being held together by screws. The whole is smoothed down in a lathe until the edges of the mica are flush with the surface of the wood. A screw of 16 threads to the centim. (40 to the inch) is cut upon the middle portion of the cylinder for a length of 45 centim. The mica is then removed from the wood, and two small holes are drilled near each of its ends. An annealed copper wire 0·19 millim. in diameter (No. 36 s.w.g.) is tightly wound around the notched portion of the mica, the turns being made to occupy alternate notches, and its ends are secured by passing them through two of the drilled holes. A second wire is then wound into the other notches, its turns alternating with those of the first. These wires constitute the electrodes, and great care is taken that they do not touch each other at any point.

The next step is to apply the selenium. A brass plate 2 millim. thick is supported upon an iron tripod and covered with a sheet of thin mica ; upon this is laid the prepared mica slip, small weights being placed upon its ends to steady it. The surface of the wired portion of the slip is evenly covered with 1 gramme (or a little less) of powdered vitreous selenium, and a small Bunsen burner is lighted beneath the brass plate. In a few minutes the greater part of the Se will melt : some of it, however, will probably crystallize, forming hard grey lumps, and when this occurs the heat must be continued, and if necessary increased, until all the grey lumps have disappeared. Then the Se is worked smoothly and uniformly over the slip with a steel spatula, particular care being taken that the surface is covered quite up to the edges. This operation is often found a troublesome one, but if the temperature be properly regulated, there is little difficulty about it. When the temperature is too low, hard crystalline lumps are formed ; when it is too high, surface-tension causes

the selenium to gather up into drops, and it becomes as impossible to spread as if it were mercury. The Bunsen flame should be adjusted so that the temperature is only just above the melting-point, 217°; the selenium then assumes a plastic semi-fluid condition and can be easily manipulated.

When a satisfactory surface has been secured, the cell is immediately removed by means of forceps and placed upon a thick copper plate to cool quickly. The Se surface should at this stage be black and lustrous, and the resistance between the electrodes sensibly infinite.

The Bunsen flame having been turned down sufficiently to lower the temperature to about 120°, the cell is replaced upon the hot plate. In a few minutes parts of its bright surface become dimmed, and shortly afterwards the whole turns a dull grey colour. The temperature is then cautiously raised until signs of melting just begin to appear, generally near one of the edges. When this occurs the burner is instantly withdrawn and the flame slightly lowered. The darkened spot recrystallizes in the course of a few seconds, and the burner is then replaced and left for four or five hours, during which time the temperature of the Se should be only a few degrees below the melting-point. Another hour is occupied in slowly cooling the cell, the flame being gradually lowered and finally extinguished. This process of long heating and slow cooling is generally spoken of as " annealing."

The resistance of such a cell as that described is generally from 50,000 to 100,000 ohms in the dark, and 50 or 60 per cent. less in diffused daylight. If alternately screened and exposed, it will with an electromotive force of 50 volts or upwards easily actuate an ordinary telegraph relay.

§ 3. *Hypothesis as to the Action of Light upon Selenium.*

Selenium as supplied commercially is never free from impurities, and indeed I have lately been informed by a distinguished chemist, who has given some attention to the subject, that perfectly pure selenium has not yet been obtained. Graham Bell states that the samples collected by him in different parts of the world were found to contain, among other things, the metals lead, iron, and arsenic.

Ten years ago I suggested * that metallic selenides, whether originally existing as impurities in the Se or formed at the expense of the electrodes during the process of " annealing," might play a very important part, not only in relation to the conductivity of crystalline Se, but also in bringing about the

* Proc. Phys. Soc. vol. vii. p. 129; Phil. Mag. August 1885, p. 178.

apparent change of its resistance under the influence of light. According to my hypothesis, the conductivity of Se depended mainly upon the selenides which it contained. I supposed the conduction to be of a truly electrolytic character, the current decomposing the selenides, and depositing upon the anode amorphous Se and upon the kathode the various metals. Amorphous Se is a non-conductor: unless, therefore, the deposited Se combined more or less freely with the metal of the anode, forming upon it a layer of conducting selenide, the resistance of a Se cell would, under the influence of a current, soon rise to infinity. It has been shown that Se does slowly unite with at all events some metals when merely brought into contact with them, and I ventured to suggest that light played its part in reducing the resistance by facilitating this union. The action would occur not only at the anode, but throughout the body of the Se, the recombination of the separated molecules of Se and the metal (forming the " Grotthuss chain ") being similarly assisted.

This hypothesis would, as I showed, explain many observed facts which could not otherwise be readily accounted for, and I adduced in support of it several arguments which need not here be repeated. But the hypothesis postulated two important assumptions which I was not able at the time (nor when I returned to the subject five years later) to justify by experimental evidence. It assumed that solid metallic selenides conduct electrolytically, and that the combination of selenium with a metal is accelerated by the action of light.

My recent experiments, some of which are discussed in the present paper, were undertaken primarily with the object of testing these two assumptions. In the course of the investigation, however, many other interesting points presented themselves for consideration, and some of the results arrived at are also here recorded. The experiments are described in the order which appeared to be most convenient ; it is of course not that in which they were actually performed.

§ 4. *The Effect of Annealing upon the Specific Resistance of Crystalline Selenium.*

The resistance of Se which has been crystallized and annealed out of contact with any metal appears to be always much greater than when metallic electrodes have been fused into it in the usual fashion. It also depends to a large extent, and in a manner which is not yet fully explained, upon the treatment which the Se has received.

Exp. 1.—A number of disks were prepared by casting Se

in a mould formed by placing a glass ring, such as is used for microscope slides, upon a glass plate. The thickness of a disk was made approximately uniform, and its surfaces polished by rubbing upon fine glass-paper laid upon a sheet of plate glass. The disk to be tested was inserted between pads of vulcanized rubber covered with tinfoil, which constituted the electrodes, and the whole was placed between hinged boards and loaded with a weight of 28 lbs. (12·7 kilos). It is unnecessary to describe the tests in detail, inasmuch as the only result arrived at was the negative one that crystalline Se has no definite specific resistance. In different tests of disks prepared from the same sample and as far as possible in the same manner, it varied from 33 megohms to 1630.

The specific resistance is certainly not always diminished, as is generally believed, by prolonged heating at a high temperature ; *i. e.* between 200° and 217°. It is indeed often increased after such an operation, as in the following extreme instance.

Exp. 2.—A disk of Se was crystallized and heated for an unrecorded number of hours in a copper air-bath at about 200°. Its specific resistance was afterwards found to be 38·5 megohms. It was again heated at the same temperature for three hours. When cold its specific resistance was 660 megohms. In both cases it was cooled slowly.

§ 5. *Action of Selenides.*

On the other hand, prolonged heating always diminishes the resistance of a Se "cell" having electrodes fused into it. This I have attributed to the action of the conducting metallic selenide which would be formed during the heating at the expense of the wires.

Exp. 3.—For the purpose of testing this conjecture, a number of cells were constructed of Se having incorporated with it cuprous selenide in different proportions. The wire used was platinum ; it was of the same gauge in all cases (0·27 millim.), and the number of turns per unit of length was also the same (10 per centim.). The surface area, however, varied somewhat, and in order to facilitate comparison the figures, as given in the annexed table, express in each case the resistance of a square centim. of surface. The light employed was always, except where otherwise stated, that derived from an 8 candle-power incandescent lamp, the filament of which was 1 ft. (about 30 centim.) distant from the face of the cell. None of the cells containing added selenide were annealed, but were cooled as soon as the Se had

crystallized. That in which there was no Cu_2Se was annealed for six hours. For comparison, the table is headed with particulars of a good ordinary copper-wire cell of similar dimensions.

TABLE I.

Composition of Cell.	Annealed or Unannealed.	Percentage of added Cu_2Se.	Resistance in dark of 1 sq. cm. Megohms.	Percentage decrease in light.
Cu Wire and Se	Well annealed	0	0·7	45 to 50
Pt Wire and Se	,, ,,	0	13·9	33
Pt wire and Se + Cu_2Se	Unannealed.	0·5	12·0	32
,, ,,	,,	1·5	14·7	57
,, ,,	,,	3	3·6	47
,, ,,	,,	4	0·90	38
,, ,,	,,	5	0·25	28

In the cell containing 1·5 per cent. of Cu_2Se, the thickness of the Se coating was accidentally made much less than the diameter of the wires, instead of equal to it, as in the other cells : hence its unduly high apparent resistance and its correspondingly great sensitiveness (for its exposed surface was disproportionately great). In other cases the results are as regular as could be expected. They demonstrate clearly enough that a cell of fairly good sensitiveness and conductivity may be formed without any annealing, if a suitable quantity of metallic selenide be first added to the Se. They also render very evident the fact that an excessive quantity of selenide, while it reduces the resistance to a comparatively low point, only does so at the cost of the sensitiveness. This agrees with the well-known fact that an ordinary Se cell whose resistance has been unduly lowered by too long heating is only moderately sensitive to light. Exactly what part is played by the free selenium remains yet to be determined ; it is certain that cuprous selenide by itself is quite insensible.

§ 6. *Sensitizing Insensitive Selenium.*

During the last fifteen years I have worked with a great many different samples of Se, and have observed that they

did not all possess exactly the same degree of sensitiveness : some were better than others, but the sensitiveness of the best was probably not more than 8 or 10 per cent. greater than that of the worst. Lately, however, I have been supplied commercially with a batch of selenium which, under the usual treatment, is almost absolutely insensitive to light. This Se differs a little in appearance from the ordinary article. In the vitreous condition its colour is of a lighter shade, and its surface is less lustrous than usual. When melted (above 217°) it forms a tenacious semi-fluid mass, which adheres like treacle to the mica and spatula and is difficult to spread ; it does not exhibit the capillary effects previously referred to, and at a suitable temperature it crystallizes with great rapidity. It has not been analysed, but such impurities as it may contain probably do not include the metallic selenides commonly met with[*].

Exp. 4.—Three copper-wire cells of the usual size were made with this Se and annealed for several hours. Their resistances in the dark had the abnormally high values of 170,000, 290,000, and 520,000 ohms respectively, the last named being very thinly coated. When illuminated by the incandescent lamp at 12 inches, the decrease of the resistance amounted in the case of the first two to only a fraction of 1 per cent. (instead of the customary 40 or 50 per cent.), and in the thinly-coated cell to about 6 per cent.

Exp. 5.—Two perfectly similar copper-wire cells of smaller size were coated, one with the insensitive Se and the other with ordinary Se, and annealed side by side for $5\frac{1}{2}$ hours. On subsequently testing, the resistance of the ordinary cell was found to be 20,500 ohms in the dark and 40 per cent. less when illuminated, while that of the other was 780,000 in the dark and only 2·5 per cent. less under illumination.

Exp. 6.—A cell was constructed having exactly the same dimensions as those last mentioned, and was coated with insensitive Se with which 3 per cent. of cuprous selenide had been previously incorporated. It was not annealed, but cooled gradually during about fifteen minutes. Next day its resistance in the dark was 190,000 ohms, and when illuminated by the lamp, 140,000, the decrease being 26 per cent.; in sunlight it fell to 43,000 ohms, or 77 per cent. less than in darkness.

Exp. 7.—Another cell of the same size was made in which

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[*] Two other samples of insensitive Se have since been supplied to me from different sources.—*June* 28th.

5 per cent. of selenide was added to the insensitive Se. Its resistance in the dark was 105,000 ohms, and when illuminated by the lamp 79,000, a fall of 25 per cent.

Exp. 8.—Another similarly sized cell had 3 per cent. of *lead* selenide mixed with the Se. Its resistance dark was 363,000 ohms, and illuminated $10\frac{1}{2}$ per cent. less.

It appears, therefore, that the addition of a small quantity of cuprous selenide imparts a fair degree of sensitiveness to the anomalous Se, at the same time bringing down its resistance to nearly the normal value. An equal proportion of lead selenide produces a similar, though less marked effect. It would be interesting to try selenides of arsenic and other metals, but I have not yet had time to do so.

It is certain that an ordinary well "annealed" Se cell with copper electrodes contains a relatively large quantity of copper selenide. Mr. W. Hibbert was kind enough to analyse the Se taken from one of my old cells to which no foreign substance had been intentionally added, and found that it contained 2·28 per cent. of combined copper, equivalent to 3·71 per cent. of cuprous selenide. Of course this must have been derived mainly from the copper electrodes.

§ 7. *Effect of Time.*

The fact that the resistance of crystalline Se with metallic electrodes fused into it decreases very greatly in course of time was first noticed by Prof. W. G. Adams and Mr. R. E. Day[*], who thought that it was due to the Se having become more completely annealed. In a former paper[†] I have suggested that the decrease is more probably to be attributed to the short-circuiting of the cell by an excessive amount of conducting selenide, formed by the gradual union of the Se with the metal of the electrodes. This view receives strong support from the following observations.

Exp. 9.—In the year 1891 I constructed a copper-wire cell but did not crystallize nor anneal the Se, which remained therefore in the vitreous state : its resistance was sensibly infinite. The cell was laid aside in a box until March 1895, when it was tested and its resistance found to have fallen to about 8 ohms. The cell was quite unchanged in appearance, the selenium surface being perfectly black and glossy. The decrease of resistance could not possibly be accounted for by spontaneous crystallization, and could hardly have been due to any other cause than the formation of selenide in the

[*] Phil. Trans. vol. clxvii. pt. i. p. 348.
[†] Phil. Mag. March 1891, p. 250.

interior. The cell was unfortunately destroyed before it occurred to me to use it for an experiment like the following.

Exp. 10.—A cell made in 1881 had then a resistance of about 100,000 ohms and was very sensitive to light. In 1895 its resistance had fallen to 10 ohms and it was quite insensitive. This was connected with a storage-battery of 26 cells, a detector-galvanometer being included in the circuit. When the current was turned on, the galvanometer-needle underwent a momentary strong deflexion and immediately returned to zero. The dark resistance of the cell was then found to have risen to 60,000 ohms, and it was once more sensitive to light. Clearly a short circuit caused by the selenide had been burnt out.

§ 8. *Action of Light in promoting the Formation of Selenides.*

Several attempts to ascertain whether the union of Se with a metal was assisted by illumination resulted indecisively. The following simple experiments are however, I think, fairly conclusive.

Exp. 11.—One side of a thick plate of copper was evenly coated with red amorphous Se by causing the fumes of boiling Se to play upon it. Half the plate was then covered and the other half exposed, first to diffused daylight and afterwards to sunlight. In diffused daylight the exposed half was perceptibly darkened in the course of two or three hours; in sunlight it quickly assumed a dark chocolate colour, the screened portion remaining bright red.

Exp. 12.—Two pieces of mica were similarly treated, but the exposed portions were not perceptibly darkened by prolonged exposure to sunlight. They became, however, covered with a slight " bloom," like that seen on a ripe plum, which I am inclined to attribute to the formation of an oxide.

Exp. 13.—A brass plate coated with red Se was exposed to sunlight in a photographic printing-frame under a design cut out of black paper and intended to represent a butterfly. A perfectly sharp and intense print of the design was produced upon the red Se. This was made on April 17 last: it has since been kept in the dark and is now exhibited to the Society.

The chocolate colour is closely matched by that of a mixture of red precipitated Se and cuprous selenide in about equal parts.

§ 9. *The Effect of Temperature upon the Resistance of Crystalline Selenium.*

Text-books and dictionaries of chemistry appear to be about equally divided upon the question whether the resistance of crystalline Se is increased or diminished by rise of temperature. There are high authorities for both opinions. In a paper published in 1883 * I gave an account of some experiments which indicated that the resistance of Se, " or rather perhaps of selenium cells," as I was careful to add, became a maximum at a certain temperature, which varied a little with different specimens but was generally a few degrees higher than the average temperature of the air. Eight different cells were tested, showing well-defined maxima at temperatures of 13°, 14°, 22°, 23°, 23°, 24°, 25°, and 30° respectively.

On further investigating the subject I have traced this curious effect to the action of the fused-in electrodes. So far as I know from a great number of experiments, a piece of crystalline Se into which wires have been fused *always* acquires a maximum resistance at a certain temperature. On the other hand, the resistance of a piece having external electrodes pressed into contact with it is *always* diminished by a rise of temperature.

Exp. 14.—A rectangular plate of Se was cast in one of the white-glazed earthenware " pans " in which moist water-colours are sold. Two platinum wires were made red-hot, and their ends embedded along the shorter sides of the rectangular plate a little below the surface. The plate was then crystallized and annealed and its surfaces smoothed with glass-paper.

The plate was suspended inside an air-bath, the bulb of a thermometer being in contact with it, and the resistance between the platinum-wire electrodes was taken at temperatures ranging from −2° to 12°. The results, which are given in the second column of Table II., indicate that the resistance was greatest when the temperature was 6°.

The same plate was then placed between two pads of india-rubber covered with tinfoil which served as electrodes, and were pressed into good contact by a weight of 500 grammes. The arrangement was placed in the air-bath, and the resistance between the opposite faces of the plate observed at various temperatures. As is shown in the third column of Table II., the resistance diminished steadily as the temperature rose.

* Phil. Mag. Jan. 1883, p. 31.

TABLE II.

Temperature. Degrees C.	Resistance between Electrodes fused into ends. Megohms.	Resistance between Electrodes pressed against surface. Megohms.
− 2	45·6	
0	48·7	
2	52·0	38 5
4	52·3	36·8
6	53·3*	34·0
8	52·5	30 2
10	49·6	26·6
12	46·7	23·9

* Maximum.

Thus with rising temperature the resistance of the *same* piece of Se appears to reach a maximum when measured between fused-in wires, and to decrease *ab initio* when measured between electrodes which are pressed upon its surface.

Beyond doubt the resistance of the Se really falls in both cases. The apparent preliminary rise when the electrodes are fused in, is due to the unequal heat expansion of the Se and of the metal. The coefficient of linear expansion of Se is twice as great as that of copper and three times as great as that of platinum. The effect of heating is to loosen the tight grip of the Se upon the metal and so to increase the resistance of the junction. The rate at which this junction-resistance increases is at first greater than that at which the specific resistance of the Se diminishes : soon, however, the latter effect predominates, and thus the resistance of the combination of Se and a metal passes a maximum.

§ 10. *Porosity of Crystalline Selenium.*

The consideration of certain phenomena, which will be referred to later, led me to believe that crystalline Se, notwithstanding its metallic appearance, must be a sensibly porous substance. Experiments were made with the view of ascertaining whether this was the fact.

Exp. 15.—One end of a brass tube was closed by a polished disk of crystalline selenium, 11·2 millim. in diameter and 1·25 millim. thick, which was tightly fixed by an indiarubber collar : to the other end was attached a glass tube which terminated in an open point about 3 millim. in diameter. The whole of the indiarubber and the edges of the Se disk were thickly coated with shellac varnish. The closed end of the tube was dipped into water and air was forced into the open end. No bubbles were formed upon the Se : if therefore Se be porous its pores must be very small.

Exp. 16.—A transpiration experiment was then made. The tube was fixed in an upright position with the Se disk at the top and the glass point at the bottom, the latter dipping into a basin of water. A wide-mouthed glass bottle was supported mouth downwards over the tube, enclosing its upper end. Coal-gas was slowly admitted into the bottle from a small nozzle. The indiarubber tube conveying the gas was for seven feet (about 2 metres) of its length coiled up in a vessel of cold water. When the gas was first admitted water rose for a short distance inside the glass tube owing to the cooling effect of the refrigerated gas : but after a minute or two it began to descend again, and soon air-bubbles were slowly but regularly given off at the pointed end. This continued until the bottle of gas was removed, when the bubbles at once ceased and the water again began to rise in the tube.

Crystalline Se is therefore sensibly porous, and no doubt absorbs moisture from the air.

§ 11. *The Polarization of Selenium by Currents.*

Among the many remarkable properties of Se which were first observed by Prof. W. G. Adams and Mr. R. E. Day in their well-known research, is the power it possesses of setting up a secondary or polarization current after being disconnected from a battery. As all who have worked much with Se must know, the opposing and ever varying electromotive force of polarization renders it very troublesome to make accurate resistance tests by the ordinary bridge method. Unless it is worth while to expend a considerable amount of time, one has to be contented with two or at most three significant figures, and even this degree of accuracy cannot be attained unless care is taken to depress the battery and galvanometer keys only for a moment [*].

[*] If the battery key be kept down for a few seconds, and after it is raised the galvanometer key be depressed, a considerable deflexion due to the secondary current will generally be observed. For exact measurements it is necessary to balance to a constantly changing false zero.

In a former communication I stated my belief that these polarization effects resulted from the electrolysis of the metallic selenides contained as impurities in the Se. Whether this be so or not, the following experiments plainly indicate that the presence of moisture is necessary for the production of the phenomenon.

Exp. 17.— The electrodes of a Se cell were connected first with the poles of a battery, and then by means of a " change-over " switch with a galvanometer : this produced a deflexion of 90 divisions, indicating an E.M.F. of rather more than $\frac{1}{100}$ volt. The cell was then placed in a glass receiver over strong sulphuric acid, the connecting wires being passed through an indiarubber stopper. From time to time it was successively joined to the battery and the galvanometer, and the polarization current was observed to be gradually diminishing. After 18 hours the deflexion was only 3 divisions. The air was then exhausted from the receiver, and 24 hours later no polarization current whatever could be detected, even after prolonged connexion with the battery. A current greater than $\frac{1}{300}$ part of that which occurred in ordinary air would certainly not have escaped observation.

Exp. 18.—The cell was afterwards suspended for an hour in a receiver over a basin of water and then tested for polarization. The spot of light was immediately deflected far beyond the limits of the scale.

Probably therefore the polarization results merely from the electrolysis of water ; in any case the presence of water seems to be requisite for its production.

It is perhaps worth noting that little if any polarization is exhibited by crystalline Se of the coarsely granular form obtained by gradually *lowering* the temperature of the molten substance, instead of by heating solid vitreous Se. The specific resistance of this form is much lower than that of the other, and its sensitiveness is also less.

§ 12. *The Effect of Moisture upon Conductivity and Sensitiveness.*

The water ordinarily present in Se, even if it had no other effect, would naturally influence its apparent conductivity by acting as a shunt or alternative path for the passage of the current. We should expect, therefore, that if a cell were made as dry as possible, its resistance would be increased, and this was found to be the case.

Exp. 19.—A cell with a Se surface measuring 4 centim. by 1·5 centim., and containing 64 turns of 0·19 millim. copper wire, was suspended in a receiver over sulphuric acid, and tests

were made of its resistance both in darkness and under
illumination by an 8 candle-power lamp at 30 centim. The
results are given in Table III.

TABLE III.

Selenium Cell in Receiver over H_2SO_4.

Time. Hours.	Resistance. Dark.	Resistance. Illuminated.	Percentage Decrease.
0	50,400	25,400	49·5
28	83,000	35,500	57·2

The dark resistance of the cell, it will be seen, increased in
28 hours from 50,400 to 83,000 ohms : if, therefore, the water
which it originally contained acted like a metallic shunt, its
resistance taken alone must have been about 128,000 ohms.
Now it was found that a thin plate of Se, after having been
dried over sulphuric acid for 22 hours, lost $\frac{1}{2800}$ part of its
weight. The weight of the Se in the cell used in the present
experiment was about 0·4 gramme ; probably, therefore, it
originally contained about $\frac{1}{7000}$ gramme of water. Knowing
the dimensions of the cell (which are given above), it is easily
calculated that if this quantity of water when uniformly dis-
tributed between the electrodes of the cell offered a resistance
of 128,000 ohms, its specific resistance must have been
approximately 7800 ohms. This is of the same order of
magnitude as the specific resistance of good distilled water,
though that of purer water is of course much higher. We
may fairly conclude, then, that absorbed moisture plays no
active part in diminishing the dark resistance of Se, but
behaves merely as if it were an inert shunt.

As regards *sensitiveness*, moisture might conceivably exert
one of four different influences. If it acted simply as a
shunt, its removal ought to increase the sensitiveness of the
cell in an easily calculable degree. If its presence were
essential to the chemical or physical change which is effected
by the agency of light, then a perfectly dry cell would
also be perfectly insensitive. If moisture, without being in-
dispensable, were yet in some degree favourable to the
operation of light, the sensitiveness of the cell, though it
might possibly be increased when the water was withdrawn,
would still not be so great as if a metallic shunt of equal
resistance had been cut out. Lastly, if the influence of

water were positively prejudicial, its removal would result in a greater increase of sensitiveness than if it had been a mere shunt.

The figures in Table III. seem to show that the presence of water, though not essential to sensitiveness, does to some extent assist the action of light. The percentage decrease of the resistance of the dried Se under illumination is considerably greater than that of the undried, but still it is not so great as it would have been if a shunt of 128,000 ohms (the resistance of the water alone) had been withdrawn. In the latter case the resistance of the dry cell in the light would have been only 31,700 ohms instead of 35,000, and the percentage decrease 61·8 instead of 57·2.

Exp. 20.—Three cells were at different times constructed, and after being kept for some hours at a temperature of about 200° were without any previous cooling transferred as rapidly as possible to the sulphuric acid receiver. All turned out to be sensitive to light while in the dry air. Unless, therefore, Se can condense moisture in its pores at a temperature of 200°, which is not probable, its sensitiveness to light is not entirely dependent upon the presence of water. Having regard to the observations detailed in the next section this was contrary to my expectation.

§ 13. *Attempted Electrolysis of Metallic Selenide.*

Many abortive attempts were made to ascertain whether cuprous selenide conducts electricity entirely like a metal, as is generally believed, or like an electrolyte, as required by my hypothesis. The experiments of which an account is given in this section appear to show that if the conduction is not altogether electrolytic, it is under certain conditions, at least partly so. It must, however, be admitted that the results, though of considerable interest, cannot be regarded as conclusive. The condition requisite for apparent electrolysis is that the surface of the selenide should be moist, a condition of course suggestive of some secondary action.

Exp. 21.—A mass of cuprous selenide about 2 millim. in thickness was placed between two platinum foil electrodes, each of which was covered with four layers of filter-paper moistened with distilled water. The arrangement was pressed together by a weight of 28 lbs. (12·7 kilos), ordinary precautions being taken to avoid short-circuiting. A current averaging 0·03 ampere was passed through the moist selenide for about four hours. On examining the papers afterwards, it was found that those which had been in immediate contact with the selenide were stained a dark grey colour, due

evidently only to transferred particles of selenide. The other papers had received stains which differed greatly in appearance according as they were upon the anode or the kathode.

On the *anode* papers the stains were scarlet, and I satisfied myself that they were beyond doubt due to red amorphous Se. For (1) stains of a precisely similar hue and character were obtained by electrolysing a solution of selenious oxide contained in a pad of filter-paper, though of course in this case the stain appeared upon the kathode. (2) The stains turned dark brown when heated. (3) They were not affected by cold hydrochloric acid, as red oxide of copper would have been. (4) Nor by sulphuric acid. (5) Nor (unless very slowly) by cold nitric acid. (6) Hot nitric acid quickly dissipated them. (7) So also did a mixture of cold nitric and hydrochloric acids. (8) The red stuff could be volatilized at a temperature below that at which the paper was scorched.

On the *kathode* papers the stains were of a dark brown, nearly black, shade, surrounded by small irregular patches of green, blue, and orange. The dark-brown stuff acquired a metallic copper-coloured lustre when burnished, which is sufficient proof that it consisted, largely at all events, of finely divided metallic copper. It was ascertained that if a little of the selenide itself were finely powdered, rubbed into moist paper and dried, no such metallic appearance was produced by burnishing.

The experiment was repeated several times with variations in the details : *e. g.* in one case the selenide was fused with an excess of Se, in another with an excess of Cu. But it was invariably found that red stains were formed at the anode, and almost invariably traces of metallic copper appeared at the kathode.

This experiment naturally led me to try to obtain electrically liberated selenium in larger and measurable quantities.

Exp. 22.—Some selenide of copper was prepared by heating together 126 parts of shredded copper-foil and 79 of crushed Se in a closed crucible to bright redness. The product was an iron-grey, cindery-looking mass.

A fragment of this was held in a brass clip, and the lower portion of it dipped into a beaker of water opposite a strip of Pt foil. The selenide was joined to the negative pole of the battery, the Pt to the positive : thus the water was made the anode in relation to the selenide. A current of 0·025 ampere was passed for half an hour. In a few minutes after starting, the water had become scarlet and quite opaque with suspended red Se. Unfortunately, however, the selenide was very friable, and numerous small particles were detached from its

surface by the hydrogen bubbles which formed upon it ; these became mixed with the liberated Se and made it impossible to ascertain the weight of the latter.

Exp. 23.—In order to obtain a more coherent substance, two parts of Se were thoroughly incorporated with one of Cu_2Se ; the mixture was then fused in an earthenware mould, and thus formed into a rectangular plate weighing 1·0731 gramme. Se itself being a very bad conductor, it was believed that practically the whole conduction would take place through the selenide. The plate was immersed in water with a strip of Pt, and a current averaging 0·023 ampere was passed for ten minutes. As soon as the circuit was closed the black plate began to give off dense red clouds ; and when it was dried and weighed after the experiment, it was found to have lost 0·0250 gramme. If the decomposition had been primarily electrolytic, the weight of liberated Se, assuming its electro-chemical equivalent to be 0·00082 *, would have been no more than about half that amount, namely 0·0113 gramme. The red Se was filtered out of the water and examined for particles of *débris*. None were detected by the unassisted eye, but under the microscope many became visible, though whether in sufficient quantity to account for the observed excess of weight is somewhat doubtful.

Exp. 24.—This was a repetition of the last, except that the plate contained six parts of Se to one of Cu_2Se (instead of two to one) and weighed 1·0223 gramme. The current, which averaged 0·016 ampere, was left on for 30 minutes. The actual loss of weight was 0·0386 gramme ; the calculated loss, according to the electrolytic law, being 0·0236 gramme. In this case, therefore, with a weaker current and a less friable mixture, the observed exceeded the calculated loss by only 64 per cent. instead of 121 per cent. as in the previous instance. The microscope again revealed the presence of numerous small black particles. The closer approximation is in favour of the possibility that the excess might have been due to the disruption of fragments of the selenide. Further experiments, which need not be detailed, leave the point still doubtful.

This effect of electrical action may be exhibited in a striking manner as follows :—A sheet of moistened filter-paper is laid upon a metallic plate, preferably of Pt, which is in connexion with the positive terminal of a 50-volt battery ; a pencil formed of one part of Cu_2Se and six parts of Se is connected

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* The electrochemical equivalent of hydrogen multiplied by the atomic weight of Se $= 0·000010384 \times 79 = 0·000820336$. Quite possibly, however, the E.C.E. of Se is only half this value.

by a flexible wire to the negative terminal.   When this black pencil is drawn over the paper, it makes a bright red mark which is immediately broken off if the current is interrupted or reversed.   If a copper plate be used, the marks will be brown instead of red.

The red stuff separated in the foregoing experiments turned black when heated, and fused and crystallized like ordinary Se.   The resistance of a small cell made from a portion of it was 65 per cent. lower than the average ; the cell was very sensitive to light, the diminution of its resistance under illumination being 53 per cent.

The question naturally presented itself, whether the separation of the red Se might not in some not easily imagined manner be due to the hydrogen liberated from the water, and not primarily to the current.

Exp. 25.—To test this a zinc wire 1·7 millim. in diameter was coated with a fused mixture of Se and Cu_2Se and immersed in dilute sulphuric acid.   The acid penetrated the pores of the coating, and soon small bubbles of hydrogen began to rise from the surface, continuing for about 5 hours.   The coating was then broken up, and it was found that all the zinc inside it had been dissolved.   A microscopic examination of the fragments failed to disclose the smallest trace of any red Se.

The experiment was repeated with the substitution of ordinary commercial Se, and the same negative result was arrived at.   It was ascertained that sulphuric acid did not dissolve the red stuff.

Exp. 26.—An experiment was arranged with the view of determining whether the current exerted any action, real or apparent, upon Se itself when unmixed with any metallic selenide except such as it might contain as an accidental impurity.

A well-annealed plate of crystalline Se having a Pt electrode fused into one edge was supported in water, the electrode being about 5 millim. above the surface.   A slip of Pt foil was also immersed, and the two were joined respectively to the terminals of a storage-battery of 26 cells.   Until the current had been passing for more than 24 hours, there was no perceptible discoloration of the water.   Shortly afterwards it was found that the plate was surrounded by a slight red deposit just above the water-line, and that the lower part of the water had become pink.   On examination, it appeared that the red stuff proceeded entirely from a small hole in the plate above the water-line : the Se was therefore broken up and the course of the hole, which was full of water, was

traced and found to terminate very near the Pt electrode, where no doubt platinous selenide existed.

This experiment, though not conclusive, tends to show that Se unmixed with selenide is not acted upon by the current. It is possible that moist crystalline Se may be converted into the red amorphous form by electrical action, but the question cannot be definitely settled until perfectly pure Se is obtainable.

§ 14. *Photoelectric Currents.*

Another of the interesting discoveries of Adams and Day was the fact that an electromotive force could be set up, and a current started in annealed Se merely by the action of light[*]. This observation has been fully confirmed by subsequent experimenters, and the belief has been expressed that the phenomenon affords an example of the direct conversion of the energy of light into that of electricity. Others have held the opinion that the effect is of a purely thermoelectric nature. My own investigations have led me to the following conclusions :—

(1) The effect is undoubtedly due to light and not to heat; or, more accurately, it is brought about by the action of radiation, and not by change of temperature.

(2) The energy of the photo-electric current is primarily of chemical or voltaic origin, and is not derived from radiation. Light merely has the effect of facilitating the chemical process, and can have no further influence when the supply of unused material is exhausted.

Exp. 27.—A rectangular plate of Se measuring $14 \times 11 \times 2$ millim. had Pt wire electrodes fused into its two ends and was "annealed" for several hours. The electrodes being connected with a galvanometer, a piece of magnesium ribbon was burnt near the Se : a deflexion immediately occurred showing a current which ceased as soon as the light was extinguished. By screening the two ends alternately, it was ascertained that the effect was produced only at one junction, the other being quite insensitive. (It may happen in different cases that both junctions are sensitive or neither. As will be shown later, sensitiveness points to imperfect electrical contact between the Se and Pt due perhaps to a film of red Se.) The direction of the current through the sensitive end was from Se to Pt.

The Se plate was afterwards placed under a glass receiver with a basin of water, and connected with the galvanometer by wires passing through a caoutchouc stopper. In a minute

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[*] *L. c.* p. 333.

or so a small current was indicated which, after slowly increasing for about 15 minutes, became constant. While magnesium was being burnt near the receiver, the strength of the current was greatly intensified ; even diffused daylight temporarily increased the deflexion to the extent of 150 scale-divisions. The direction of the current was as before from Se to Pt.

The plate was then enclosed in a receiver over sulphuric acid. In 8 minutes the permanent current had completely disappeared, and exposure to diffused daylight caused a deflexion of only 2 divisions. In 20 minutes burning magnesium at a distance of 6 inches failed to produce any effect whatever. The Se had completely lost its power of generating a current under the influence of light.

The natural inference seems to be that Se (or Se containing selenide) is slowly oxidized by water, and that the oxidation is increased by the action of light[*]. Some points bearing on the question will be further considered in the next section.

§ 15. *The Thermoelectric Quality of Annealed Selenium.*

Adams and Day believed they had obtained evidence that the thermo-electric quality of crystalline Se was altered by prolonged annealing. To use the old-fashioned terminology, they thought that by the process of annealing Se was raised from its place at the bottom of the thermo-electric series, which the experiments of Matthiessen had assigned to it, to a position somewhere above that of platinum. In other words, if a Se–Pt junction were heated to a temperature slightly above that of the other junctions in the circuit (the latter being at the ordinary temperature of the air), then, if the Se were crystallized but not thoroughly annealed, there would be a current from Pt to Se through the heated junction, but if the Se were well annealed the thermo-current would be in the reverse direction—from Se to Pt.

They applied heat at a junction by directing upon it a blast of hot air from a glass tube terminating in a fine nozzle, the tube being heated over one or more Bunsen burners. Where it was possible, heat was also applied by holding the junction

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[*] Later experiments render this doubtful. With Se which does not contain any considerable admixture of Pt_2Se (and perhaps it should be added, which has not been previously used as an anode) the photo-electromotive force appears to be always in the *opposite* direction—from Pt to Se. And this seems to be the case not only with water as the electrolyte, but also with the other badly conducting liquids, such as œnanthol, used by Prof. Minchin.—*June* 28th.

of Pt and Se between the finger and thumb. All the pieces of Se with which they worked had had Pt wires fused into their ends before being annealed.

The following experiments point to a conclusion different from that of Adams and Day.

Exp. 28.—Experiments were made with three different specimens of Se, all of which had been annealed for many hours. None of these had electrodes fused into them. The arrangements were varied in details, and the Pt–Se junctions heated in different ways. In all cases the direction of the thermo-electromotive force was from Pt to Se across the hot junction. The direction of the current was not affected by the addition of platinous selenide to the Se.

Further experiments were made with the Se plate referred to in the preceding section which had Pt wires fused into its ends.

Exp. 29.—The Pt wires being connected with the galvanometer, it was found that when one junction was touched with the finger there was as usual a current from Pt to Se, but that when the other was touched (that which had generated the photo-electric currents in a former experiment) there followed a current in the opposite direction—from Se to Pt.

All the following observations were made with this anomalous junction.

Exp. 30.—The junction was heated by touching it first with the pointed tip of a warmed glass rod and afterwards with a hot copper wire. In both cases there resulted a current in the *normal* direction—Pt to Se.

Exp. 31.—A bent glass tube having a fine nozzle at one end was heated over a Bunsen flame, and air was blown through it from the mouth upon the junction. Result, an *abnormal* current—Se to Pt.

Exp. 32.—The last experiment was repeated, but the air was driven through the tube by a foot-blower. Result, *normal*—Pt to Se.

Exp. 33.—The tube was allowed to cool, and when quite cold air from the lungs was again blown through it. Result, a current from Se to Pt stronger than that obtained with the hot blast in Exp. 31.

Exp. 34.—A small piece of sponge moistened with tepid water was held upon the end of a wire near the junction but not touching it. There immediately followed a small current from Se to Pt.

In short, the anomalous current from Se to Pt was in every case clearly started, not by heat but by moisture.

The succeeding experiments indicate that at the anomalous junction the electrical contact between the Pt and Se was imperfect, and that the Se contained a certain amount of platinous selenide.

Exp. 35.—One part of platinous selenide having been incorporated with six parts of Se, the mixture was fused and crystallized. Thus was obtained a button of crystalline Se containing about 15 per cent. of platinous selenide. The button and a piece of Pt foil were partly immersed in water and their dry ends connected to the galvanometer. A voltaic current was indicated from the button to Pt through the water.

Exp. 36.—The button was dried and tested for a thermo-current with Pt. Result, current from Pt to button through the junction. The button, therefore, behaved thermo-electrically like ordinary Se.

Exp. 37.—By means of an adjustable spring a strip of Pt foil was arranged so as to press lightly on the button. The two were connected with the galvanometer.

Touching the button near the junction with a hot wire caused a current from Pt to button.

Holding the tip of the finger very near the junction without actual contact caused a current from button to Pt.

Blowing air upon the junction from a hot glass tube produced a current from Pt to button when the air-blast was derived from a foot-blower, and from button to Pt when air from the lungs was blown through the hot tube.

Thus all the thermo-effects of the "anomalous" junction were completely imitated. Perhaps in the case of that junction good contact was prevented by a film of non-conducting red Se, or possibly the wire electrode may have been simply loose.

These effects could not be produced when using a button which consisted of Se annealed without contact with a metal and containing no added selenide, the voltaic effect being then similar in direction to the heat-effect.

Summary.

1. The conductivity of crystalline Se appears to depend principally upon the impurities which it contains in the form of metallic selenides. It is suggested that the selenides conduct electrolytically, and that the influence of light in increasing the conductivity is to be attributed to its property of facilitating the combination of selenium with metals in contact with it.

2. The specific resistance of crystalline Se has no definite value but is always very high, varying in the specimens tested from about 30 to 1600 megohms. It is not in general diminished by prolonged heating unless the Se is in contact with a metal (Exps. 1, 2).

3. A Se cell having Pt electrodes and made with Se to which about 3 per cent. of cuprous selenide has been added, is, even though unannealed, greatly superior both in conductivity and sensitiveness to a similar cell made with ordinary Se and annealed for several hours. It is not, however, quite equal to a cell prepared in the usual way with copper electrodes (Exp. 3).

4. A particular sample of commercial Se which, when treated in the ordinary manner, was almost absolutely insensitive to light, was rendered sensitive by the addition of a little metallic selenide (Exps. 4–8).

5. The great fall of resistance exhibited by pieces of Se with fused-in electrodes after the lapse of a few years, is not due to any material lowering of the specific resistance of the Se, but to short-circuiting by selenide formed at the expense of the electrodes. The resistance of an old cell was instantly raised from 10 ohms to 60,000 by connecting it with a 52-volt battery and thus burning out the short circuit (Exps. 9, 10).

6. Red Se in contact with copper or brass is quickly darkened by the action of light, owing, it is suggested, to the formation of selenide. Photographs may be printed on copper or brass coated with red Se and preserved in darkness for a long time (Exps. 11–13).

7. The resistance of crystalline Se always decreases with rise of temperature. The apparent increase of resistance on heating generally observed when the electrodes are fused into the substance, is to be explained by the fact that the heat-expansion of the Se is much greater than that of the metallic electrodes; imperfect contact is consequently produced at the junction (Exp. 14).

8. Crystalline selenium is porous and absorbs moisture from the air (Exps. 15, 16).

9. The polarization of Se after being traversed by a current is due to absorbed moisture (Exps. 17, 18).

10. The moisture ordinarily present in Se renders the apparent resistance much lower than the true resistance of the substance (Exp. 19).

11. The presence of moisture is not essential to sensitiveness, but appears to be in a slight degree favourable to it (Exps. 19, 20).

12. When a current is passed through cuprous selenide between platinum electrodes which are covered with moistened paper, red Se is deposited on the anode paper and metallic copper on the kathode paper (Exp. 21).

13. If cuprous selenide is made the kathode and a strip of Pt the anode in water, red Se mixed with detached particles of the selenide is deposited in the water (Exp. 22).

14. With a mixture of cuprous selenide and Se the quantity of detached black particles is greatly diminished, but the weight of the separated red Se appears to be greater than that required by the law of electrolytic decomposition. Possibly the current has the effect of converting pure crystalline Se when moistened into the red amorphous variety (Exps. 23, 24).

15. The hydrogen produced by the action of zinc upon dilute sulphuric acid has no effect upon the cuprous selenide nor upon Se in contact with the zinc (Exps. 25, 26).

16. The photo-electric currents sometimes set up when light falls upon Se are dependent upon the presence of moisture and are no doubt of voltaic or chemical origin. (Exp. 27).

17. Experiments which have seemed to place well-annealed selenium above platinum in the thermo-electric series were vitiated by the presence of moisture. Dry Se is always below Pt (Exps. 28–37).

XX. *The Measurement of Varying Currents in Inductive Circuits. By* Alfred W. Porter, *B.Sc., Demonstrator of Physics, University College, London, and* David K. Morris, 1851 *Exhibition Scholar, University College, London* [*].

THE following paper describes an application of the principle of the potentiometer to the measurements of rapidly varying (but not alternating) differences of potential; and hence, to the measurement of the currents to which they give rise: a problem which presented itself in the course of an investigation into the propagation of magnetic induction in iron which was begun more than a year ago. This investigation we hope shortly to publish.

A non-inductive resistance r (fig. 1) is connected in series with a magnetizing coil the current in which we desired to measure; so that the potential difference between the terminals of r is at any instant a measure of the current in the coil. When the current is steady, this difference of potential can

be measured by the ordinary compensation or potentiometer method ; but when it is varying a modification of the method is required. The usual galvanometer is replaced by one provided with stops, so that the needle system is free to turn in one direction only. Let now the strength of the current rise continuously, the slider C meanwhile making contact with the potentiometer wire at such a point that " balance " occurs for

Fig. 1.
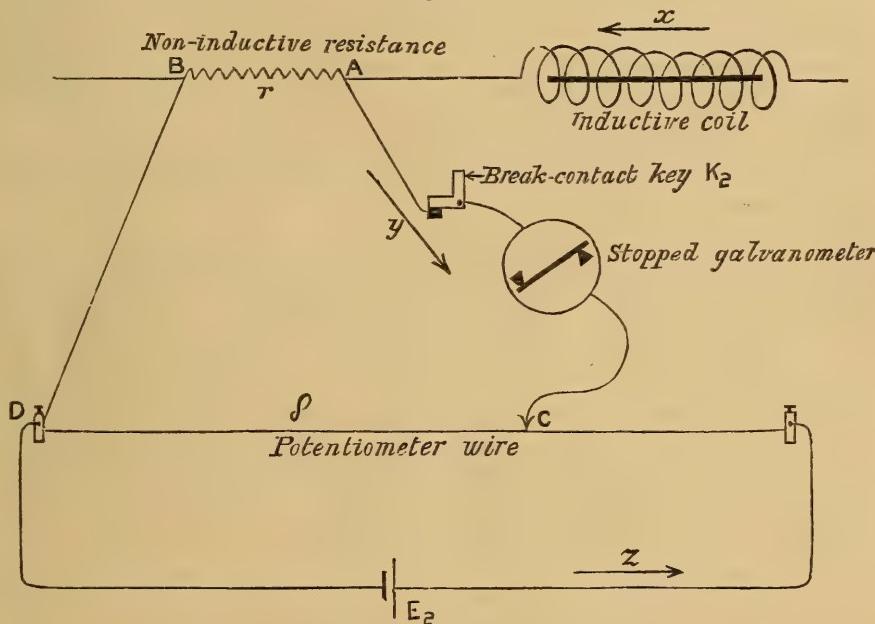
a particular value of the current. There will then be a current in the galvanometer which changes sign at the instant of potentiometer balance ; and if the galvanometer terminals are so connected that the initial current in it forces the needle against the stops, the needle will begin to fly off just as this current passes through zero. Therefore if the galvanometer circuit be broken at or before this instant no throw of the needle is produced ; it is clear then that either by altering the time interval during which the current is permitted to flow through the galvanometer, or by adjusting the position of the slider, the throw can be reduced to zero; and the fall of potential (*e*) between the points C and D (fig. 1) would be equal to the fall down the non-inductive resistance if it were not for the self-inductance Λ of the galvanometer. We have in fact for each balancing position of the slider

$$rx = e + \Lambda \overline{\frac{dy}{dt}}\bigg|_{y=0} \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (1)$$

where $\overline{\dfrac{dy}{dt}}\Big|_{y=0}$ is the rate of change of the galvanometer current at the instant when it passes through zero, and x is the instantaneous value of the current in the coil at that instant. It is therefore necessary to evaluate $\overline{\dfrac{dy}{dt}}\Big|_{y=0}$ for each value of e. Let g be the resistance from A to C (through the galvanometer) together with that of the lead from B to D, and p the total resistance of the potentiometer circuit, *i. e.* of the slide wire and the cell (E_2) ; let ρ denote the resistance of the portion CD of the slide wire ; and let the currents be as shown in the figure (fig. 1).

The general equations which must be satisfied at every instant are

$$\Lambda\frac{dy}{dt} + (g+r+\rho)y + \rho z - rx = 0,$$

and

$$pz + \rho y = E_2.$$

Now the normal current in the slide wire is $\dfrac{E_2}{p}$ and $\dfrac{E_2\rho}{p} = e$ the difference of potential recorded for a position of the slider corresponding to a resistance ρ. Hence, eliminating E_2 and z, the general equation becomes

$$\Lambda\frac{dy}{dt} + \left(g+r+\rho-\frac{\rho^2}{p}\right)y = rx - e. \quad \cdots \quad (2)$$

If this equation is differentiated with regard to t and solved for $\dfrac{dy}{dt}$, putting

$$\frac{g+r+\rho-\dfrac{\rho^2}{p}}{\Lambda} = \alpha,$$

we obtain

$$\frac{\Lambda}{r}\frac{dy}{dt} = \epsilon^{-\alpha t}\int_0^t \epsilon^{\alpha t}\frac{dx}{dt}\,dt.$$

Since when $t=0$, $\dfrac{dy}{dt} = 0$. This last statement follows from the fact that at the initial instant there is no abrupt change in the fall of potential between A and B.

Now at the instant of balance τ for which $y=0$, equation

(2) reduces to equation (1) which is $\Lambda \left.\dfrac{\overline{dy}}{dt}\right|_\tau = rx_\tau - e$; or by substitution

$$\frac{e}{r} = x_\tau - \epsilon^{-a\tau} \int_0^\tau \epsilon^{at} \frac{dx}{dt} \, dt.$$

This has to hold for each successive value given to e, and the corresponding value of τ; it is therefore a running equation between e and τ, and we may differentiate it with regard to τ. Strictly speaking, α is now a variable, since to different balancing instants there correspond different values of ρ; but the quantity $\rho - \dfrac{\rho^2}{p}$ which occurs in α cannot exceed the value $\dfrac{p}{4}$, so that the extreme variations of α can always be kept small by using a galvanometer whose resistance is high compared with that of the slide-wire employed (in our experiments it did not vary more than 1 part in 700). We shall therefore treat it as a constant; we then obtain by differentiation

$$\frac{d\left(\dfrac{e}{r}\right)}{d\tau} + \alpha \, \frac{e}{r} = \frac{dx_\tau}{d\tau} + \alpha \acute{x}_\tau - \frac{dx_\tau}{d\tau},$$

or

$$x_\tau = \frac{e}{r} + \frac{1}{\alpha} \frac{d\left(\dfrac{e}{r}\right)}{d\tau}, \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (3)$$

which gives the actually occurring coil current in terms of e, the experimentally obtained function of τ.

It should be observed that at the instant of balance, the coil circuit and potentiometer constitute electrically unconnected circuits, hence at that instant the coil current is unmodified by any contribution from the potentiometer; previous to the balancing instant, however, the galvanometer which forms the connecting link between the two conveys a gradually diminishing current, and effects thereby a corresponding though very small change in the value of the current in the coil.

Now we saw that α might be regarded as a constant, and in that case its value is simply $\dfrac{r+g}{\Lambda}$: hence, when the quantities $\dfrac{e}{r}$ have been plotted against their time intervals τ, all that is necessary is to multiply the slope of the curve thus obtained

by $\dfrac{\Lambda}{r+g}$ and add the result to the existing ordinate at that point.

Dr. Sumpner has pointed out (Phil. Mag., 1888, vol. xxv. p. 470) a simple construction by means of which equations of the above form (3) can be graphically solved.   The following is a convenient method of applying this construction :—

AA′ (see fig. 2) is the given function, which in the present case is $\dfrac{e}{r}$ plotted in amperes upon a time base, and BC is any ordinate ; if then a length CD, equal to the actual value of

Fig. 2.
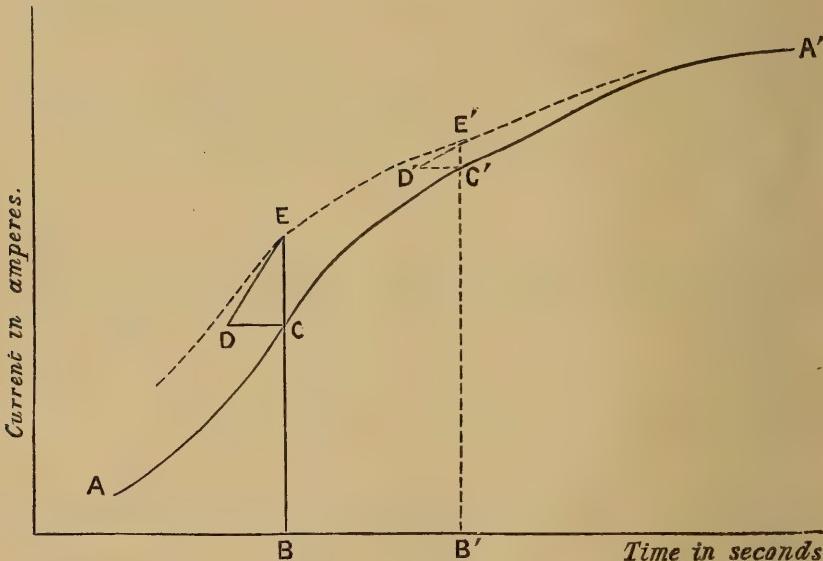
$\dfrac{\Lambda}{r+g}$ in seconds, be measured off from C towards the left, and a line DE be drawn parallel to the direction of the curve AA′ at C, we have at once

$$EB = EC + CB$$

$$= CD\,\frac{EC}{CD} + CB$$

$$= \frac{\Lambda}{r+g}\,\frac{d\left(\dfrac{e}{r}\right)}{d\tau} + \frac{e}{r} = x,$$

and in this way any number of points can be obtained on the required current curve (indicated on the figure by a dotted line). The process is exceedingly simple, especially when, as would usually be the case, the $\left(\dfrac{e}{r}, \tau\right)$ curve is plotted on squared paper.

It is preferable to maintain the current in the slide-wire, by frequent standardization with the aid of a Clark cell, at such a value that the quantities $\dfrac{e}{r}$ (and not necessarily e, as in ordinary potentiometer practice) can be read off in amperes direct, making correction if needful for any lack of uniformity in the slide-wire.

The chief difficulty which must be met if the method is to be successfully employed lies, as might be expected, in the use of the stopped galvanometer ; and it was only after many experiments that we succeeded in making one which answered the required conditions satisfactorily.

The points to be borne in mind when designing such a galvanometer are the following :—

(1) A sudden removal of the couple pressing the needle against its stops should not produce a throw.

This requires that *both* ends of the needle be provided with stops ; and also that the needle shall be stiff to resist the distorting action of couples acting in a horizontal plane ; and if the arm is not formed of the magnetic needle itself, it requires that the two be rigidly connected together.

(2) The needle must not adhere to its stops even to the slightest extent, since this would prevent the smaller throws from taking place.

This condition is a most important one. We at first tried a pair of glass stops, but the needle always adhered slightly, and we traced this with some difficulty to the presence of moisture. We then carefully dried and replaced them in the galvanometer together with a small vessel containing calcium chloride. We found, however, that clean, dry, glass stops almost invariably possessed a slight electrostatic charge, the effects of which were sometimes as bad as those of moisture ; and stops made of shellac or of sealing-wax—substances not nearly so hygroscopic—were nevertheless unsatisfactory, apparently from this cause. Metal stops were tried, but they all seemed to be covered with a slight film of moisture which even a drying agent could not be relied upon to entirely remove.

The material which we ultimately adopted was *steatite* or

soapstone. This substance, curiously enough, was found very much more satisfactory than any we had previously tried. Even the effects of moisture, when no efforts were made to remove it, were comparatively insignificant (though calcium chloride was always used to obtain the best results) ; and it will take a smooth or even a polished surface, which can be renewed at any time if necessary by lightly scraping it.

    (3) The effect of slight tremors on the throws of the needle should be minimised.

In an ordinary suspended needle-galvanometer resting upon a firm support, the only kinds of oscillations which are capable of accumulating to any appre­ciable extent are those produced by a vertical vibration of the suspension. But a simple vertical vibration is unstable in a freely sus­pended body, and tends to resolve itself into an oscillation about the horizontal axis of least moment of inertia (fig. 3), which, in a reflecting galvanometer, gives rise to the up-and-down motion of the spot of light which is so apt to occur. Hence the two points where the needle rests against the stops should be points on the horizontal axis of least moment of inertia.

Fig. 3.

This is conveniently accomplished by making the needle symmetrical as far as possible about its longitudinal centre-line, and then placing the stops so as to touch the needle on this line. It was found that the throws from the stops of a needle so constructed were reliable even when it was oscillating so as to produce a violent vertical movement of the image of a scale re­flected from the mirror into a telescope.

    (4) The field at the needle due to given difference of potential between the terminals of the instrument should be as large as is consistent with the high resistance which previous considerations have shown to be necessary.

There are many advantages in stopping the needle at a long radius from the axis of suspension, in spite of the slightly increased moment of inertia which must result from so doing : perhaps the chief of these is that a comparatively small angular movement will then suffice to get the needle quite clear of its stops. Besides this, however, small to-and-fro vibrations of either of the stops impart less angular velocity to the needle ; and the coils of the galvanometer can be made

more efficient if the arms of the needle are long enough to allow of the stops being placed outside the space in which useful turns of wire can be wound.

The instrument which we designed, and which was constructed by one of us according to the foregoing principles, is shown in figs. 4 and 5. The figures explain themselves,

Fig. 4.
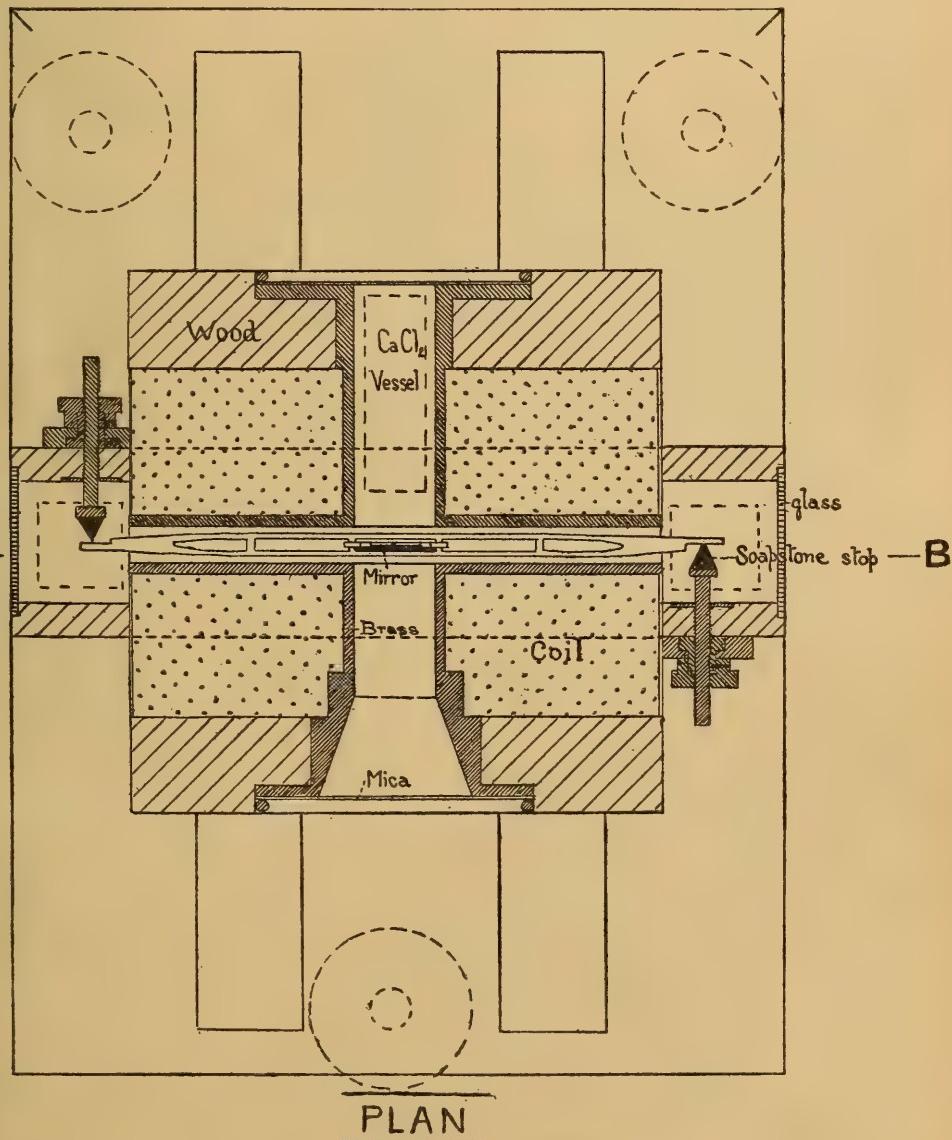
PLAN

except perhaps with regard to the construction of the needle. This is shown in plan in fig. 5, and again in back and end

Fig. 5.

glass

Aluminium arm
of needle

CaCl₂

Radial slit

Levelling screw

CROSS-SECTION **AB**   FRONT   ELEVATION
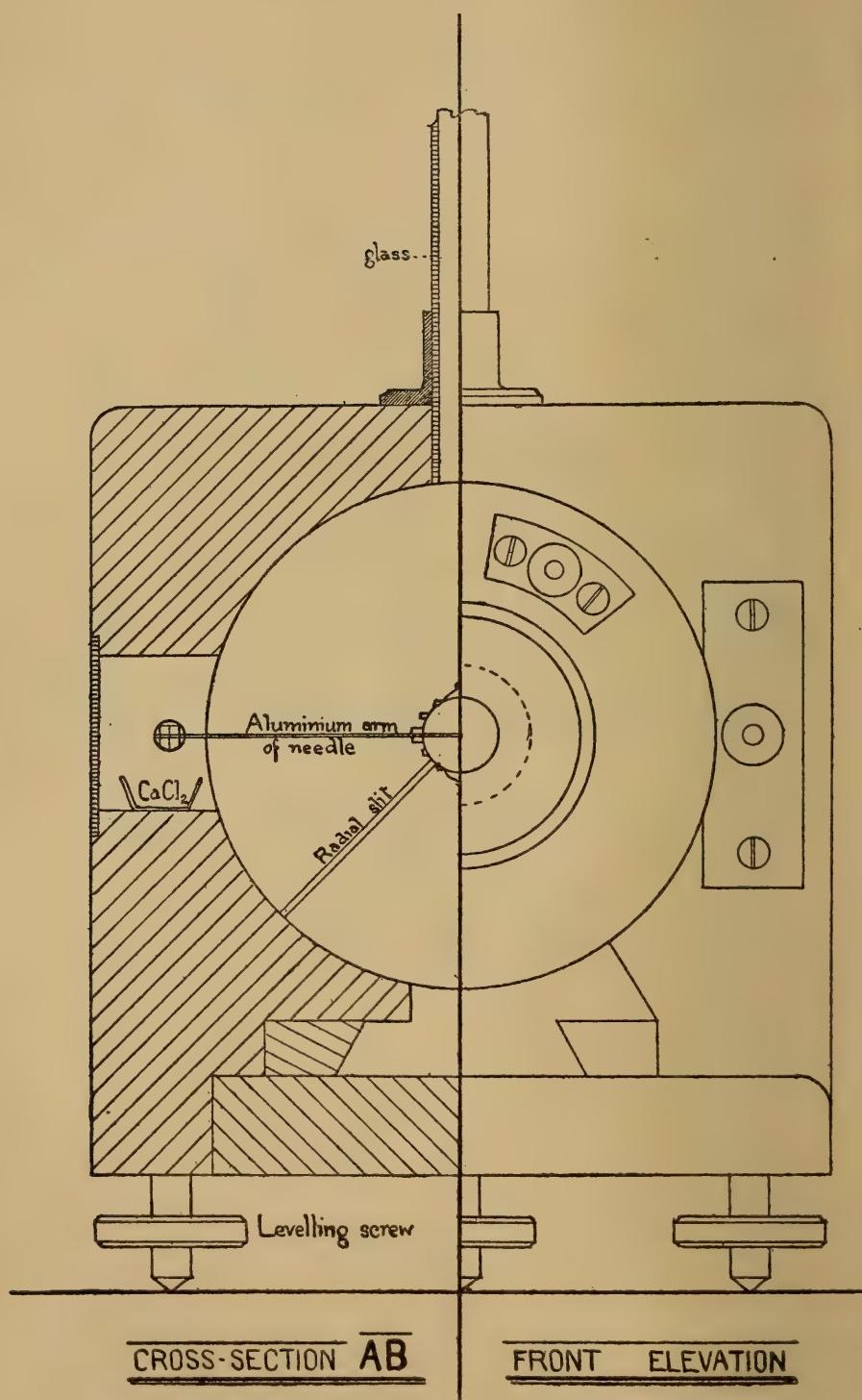
elevation in fig. 6. The mirror, the system of six magnets, and the aluminium arm are formed into a rigid system by being tied together with thin wire.

Fig. 6.
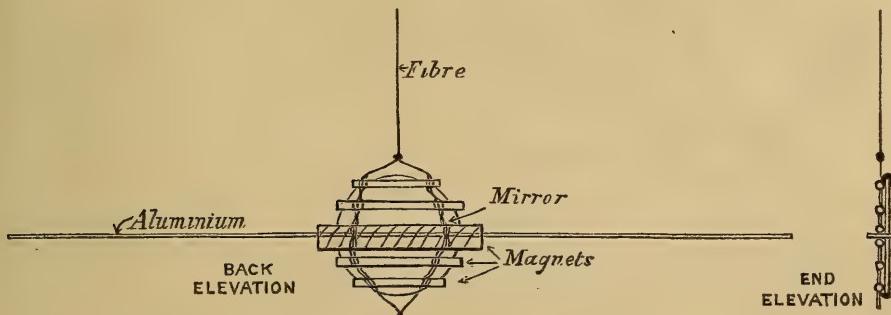
It will be noticed that the angular motion of the needle is narrowly restricted. The instrument is, however, intended for use in a " zero " method, and a very small range is all that is necessary.

When setting up the instrument for use, there are two points which must be particularly attended to :—

(*a*) The needle when freely turning must touch the two stops *simultaneously*; and

(*b*) it must *only just* be kept in contact with its stops when no current is flowing in the coils.

The following is the way in which we perform these adjustments :—The instrument, having been approximately levelled and the stops roughly adjusted, a magnet is brought near so as to make the needle press lightly against them. Under these circumstances we find that the movements of the reflected spot of light or, better, of the image in a telescope, afford a most delicate and satisfactory criterion as to whether the adjustment is perfect. An incessant though slight pendulous motion of the needle is observed as long as it rests on one stop only : this movement suddenly and entirely disappears as soon as the adjustment is perfect; this adjustment is most conveniently effected by means of the front levelling-screw alone. Finally, the magnet which was brought near is gradually withdrawn until the needle just ceases to press against its stops, and the adjustment is then complete.

Fig. 7 is an example (reduced from a drawing on a much larger scale) of curves obtained by this method. It shows both the actually observed points on an $\left(\dfrac{e}{r}\right)$ curve and also the current-curve derived from it. This is the current which occurs on reversing the impressed potential difference at the

Fig. 7.
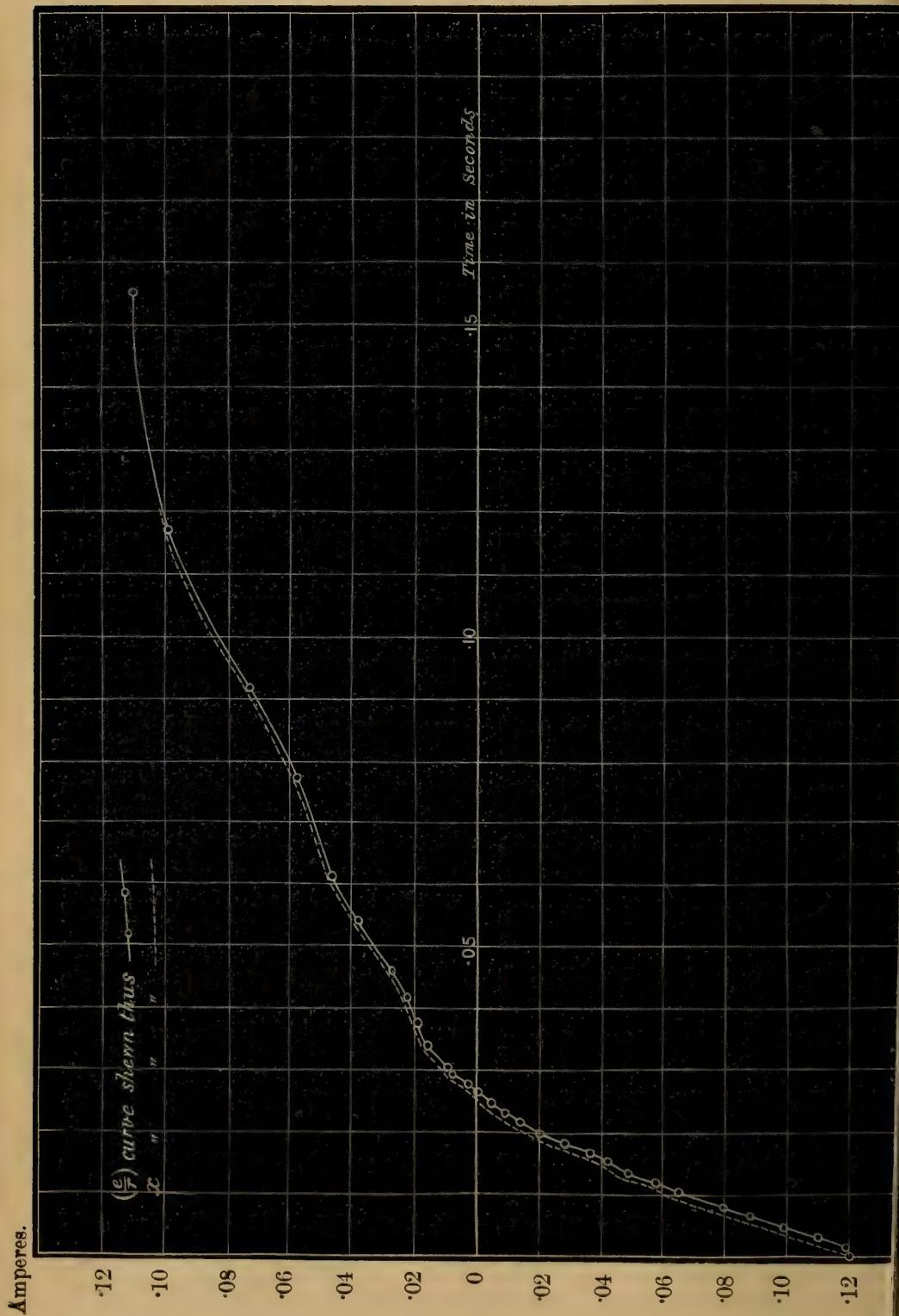
terminals of a magnetizing coil containing a core of fine iron wire. The full discussion of these curves must be reserved until the publication of the investigation to which they properly belong. It is only necessary to point out in this place that the irregularities which appear in them, and on the larger drawing from which they are reduced, are not due to accidental error, since identical experimental curves are

Fig. 8.
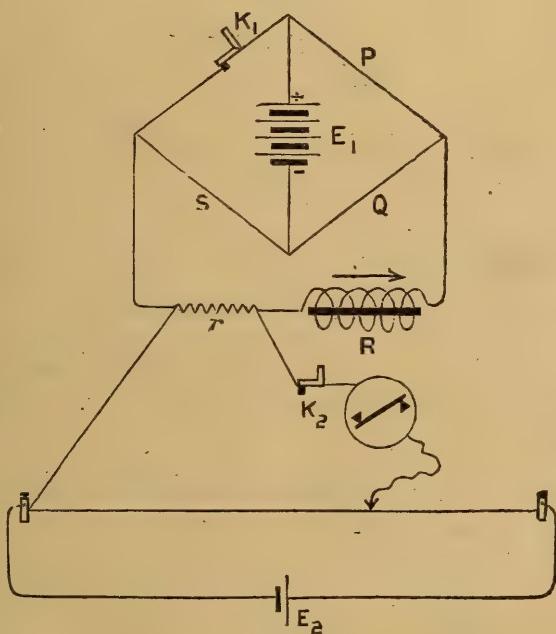
obtained on repetition; their origin must be sought for in the physical nature of the circuit through which the current flows.

The reversal of the current was effected by connecting the magnetizing coil, as shown in fig. 8, in a network similar to Wheatstone's bridge. The resistances P, Q, S were so chosen that on breaking one arm of the circuit by means of the key K_1, the current in the coil changed to a final value equal and opposite to its value before the break was made. This method effects reversal in a perfectly definite manner. It should be further noticed that if there is no inductance except that of the coil, no spark can pass when the arm is broken. The break-circuit keys referred to form part of a Helmholtz pendulum interrupter, by means of which the time interval between the instants of rupture is accurately obtained.

In the foregoing paper we have given an account of the application of the method to the measurement of a fall of potential down a *non-inductive* resistance: the method is,

however, equally applicable to the measurement of the differ-
ence of potential between the terminals of an *inductive* resist-
ance, and has in fact been used by us for such measurements.
The difference of potential (v) in such a case is given in terms
of the observed quantity (e) by the relation

$$v = e + \frac{1}{\alpha'} \frac{de}{dt},$$

where

$$\alpha' = \frac{g + \rho - \dfrac{\rho^2}{p}}{\Lambda};$$

a formula which is derived by reasoning similar to that
employed above.

Physical Laboratory,
University College, London.

XXI. *On the Refraction and Dispersion of Liquid Oxygen, and
the Absorption Spectrum of Liquid Air.   By* Professors
Liveing *and* Dewar[*].

IN August 1892 we published in this Magazine (vol. xxxiv.
p. 208) a measure of the refractive index of liquid
oxygen at its boiling-point for the yellow sodium rays, made
by means of a prism.   In the following year (vol. xxxvi.
p. 330) we published a measure of the same quantity made
by a different method.   For the reasons stated, we could only
obtain measures more or less approximate to the truth.
Since then we have made several attempts, but hitherto in
vain, to make hollow prisms with vacuous jackets, in which
the liquid oxygen could be kept in a tranquil state while
the observations were going on.   We have also attempted
unsuccessfully other methods of taking the measures.
   The chief difficulties which we encountered in making our
former measures arose from the irregularities and striations of
the glass vessels, and from the continual ebullition of the liquid
oxygen.   These difficulties have now been to a great extent
obviated.   We have come back to the method we used in
1893, which we then described as the method of MM. Terquem
and Trannin, but which had previously been suggested by
Prof. E. Wiedemann (*Archives de Genève*, li. p. 340, 1874).
However, for the cylindrical vessel before used we substituted
a globular vessel having the inside of its vacuous jacket

silvered all over except a narrow vertical strip about 4 millim. wide, which was left unsilvered to allow of the passage of light. This vessel was used, exactly as the cylindrical vessel had been used in the former experiments, as a lens by which an image of a source of light was thrown on to the slit of a spectroscope. The pair of glass plates, separated by a thin stratum of air and fixed to a rod which was the prolongation of the vertical axis of a theodolite, were arranged at about the centre of the globe. The oxygen in the globe was very tranquil, and the silvering cut off all light which did not pass nearly centrally through the globe. The result was that the light of the rays observed was cut off, when the glass plates were turned through the proper angle, much more sharply than before, and the measures are so much the more trust-worthy.

We found the spark between cadmium electrodes a convenient source of light, both because the rays are bright, and because they are dispersed through a considerable range in the visible spectrum, and it was possible to watch their extinction one after another as the glass plates were slowly turned. Even with this arrangement, the extinction of the rays when liquid oxygen was in the globe was not quite so sharp as when the experiment was made with alcohol. This was probably due to the scattered light from the bubbles in the oxygen, and was more troublesome in regard to the brightest rays.

We obtained as the mean of several observations for the blue ray of cadmium, $\lambda 4416$, $\mu = 1\cdot 2249$; for the red ray, $\lambda 6438$, $\mu = 1\cdot 2211$; for the green ray of thallium, $\lambda 535$, $\mu = 1\cdot 2219$. Also by using a flame we obtained for the red ray of lithium, $\lambda 6705$, $\mu = 1\cdot 2210$, and for the yellow rays of sodium, $\lambda 5892$, $\mu = 1\cdot 2214$.

The last figure is less than we had found in 1892 by the prism method, which was $1\cdot 2236$, and still less than that found in 1893, which was $1\cdot 226$. It is also less than that recently found by Olszewski and Witrowski (*Bull. de l'Acad. de Cracovie*, July 1894, p. 246), which was between $1\cdot 2222$ and $1\cdot 2235$. The values we have now found for the refractive indices corresponding to the red ray of lithium and the green ray of thallium are also less than those found by Olszewski and Witrowski, which were about $1\cdot 2213$ and $1\cdot 2235$ respectively. We think, however, that our measures for the red and blue rays of cadmium are better than those made for the thallium and sodium rays.

These give for the mean green nearly $\mu 1\cdot 222$, and, taking the density of oxygen at its boiling-point as $1\cdot 137$, the refraction-

constant by Gladstone's formula becomes $\dfrac{\mu-1}{d}=0\cdot1953$, and by Lorenz's formula, $\dfrac{\mu^2-1}{(\mu^2+2)d}=0\cdot1242$.

Taking Regnault's value for the density of oxygen gas at 0° and 76 centim., viz. 0·00143, and Mascart's value for the mean refractive index, viz. 1·000271, we find for gaseous oxygen the refraction-constant

$$\frac{\mu-1}{d}=0\cdot18947$$

and
$$\frac{\mu^2-1}{(\mu^2+2)d}=0\cdot12631.$$

It will be seen that this last is nearly equal to the refraction-constant as above determined for the liquid.

In Mascart's paper " Sur la Refraction des Gaz" (*Annales L'Ecole Normale Expérimentale,* 1876) some observations on the Dispersion of Oxygen and other Gases were given, which enable a comparison to be made between this property in the gaseous and liquid states. Taking Cauchy's formula

$$n-1=a\left(1+\frac{b}{\lambda^2}\right),$$

then
$$\frac{n'-n}{n+1}=b\,\frac{\dfrac{1}{\lambda'^2}-\dfrac{1}{\lambda^2}}{1+\dfrac{b}{\lambda^2}}.$$

From this b is calculated by Mascart, and is called the Co-efficient of Dispersion. The blue and red cadmium lines represent the extremest difference of wave-lengths employed. This gave for oxygen the maximum and minimum values 0·0049 and 0·0078, and a mean value 0·0064 for the Constant of Dispersion. Taking the values for the liquid state given above, the value of b becomes 0·0064. It seems possible, therefore, that the Dispersion Constant in the liquid state is identical with that of the gas.

In a recent conversation with M. Cornu about the absorption-spectrum of liquid oxygen, he suggested that it would be interesting to ascertain whether the diffuse absorption-bands were equally well developed when the increased density of the oxygen was produced by reduction of temperature at atmospheric pressure as when the gas was compressed at higher temperatures.

M. Janssen has found that the intensity of these diffuse

bands increases as the square of the density of the oxygen, and has recently confirmed this (*Comptes Rendus,* June 17, 1895) by observations of the solar spectrum in the desert of Sahara. This law, as we have already pointed out (Proc. Roy. Soc. vol. xlvi. p. 228), seems to indicate that these particular bands are due either to complex molecules generated by condensation, or to the encounters between molecules of ordinary mass which are more frequent when their free path is diminished.

To answer M. Cornu's question, we obtained liquid air directly from the atmosphere by the cold due to the rapid evaporation of liquid oxygen under reduced pressure. The method and apparatus have already been described by Professor Dewar (Proc. Roy. Inst. 20th January, 1893).

The absorption of this liquid air in a thickness of 1·9 centim. was then directly compared with that of liquid oxygen in a thickness of 0·4 centim. The light which had passed through the latter was, by means of a reflecting prism, brought into the field of view of the spectroscope at the same time with that which had passed through the liquid air. The positions of the lamps were then adjusted so that the brightness of the spectra in those parts where there were no absorption-bands was equal in the two spectra. Under these circumstances, it was seen that the absorption-bands were very much more strongly developed by 0·4 centim. of liquid oxygen than by five times that thickness of liquid air.

The vessels containing the liquids being open, the liquid air gradually evaporated; and as the boiling-point of nitrogen is lower than that of oxygen, the former evaporated more quickly, and the residual liquid contained a larger and larger percentage of oxygen. As this happened the absorption-bands became more intense, until they exceeded in strength those of the thinner stratum of liquid oxygen.

Another sample of air liquefied as before was rapidly mixed with an equal volume of liquid oxygen, and the absorption of this liquid compared, as before, with that of liquid oxygen. It was seen that the absorption of 2·4 centim. of the mixture was much greater than that of 0·4 centim. of liquid oxygen. The density of the oxygen in the mixture was in fact three times that of the oxygen in pure liquid air, and by Janssen's law the absorption should have been increased ninefold. Our observations accord with this so far as they go. Also these observations agree well with the theory of the continuity between the gaseous and liquid states. It must be borne in mind that air boils at a lower temperature than oxygen, so that the two liquids compared were not at the same temperature

by some ten degrees. Now if the diffuse absorption-bands of oxygen are produced by the molecules during their encounters with each other in the gaseous and in the liquid states, it might well be supposed that they would be profoundly modified when the oxygen assumed the solid state. Hitherto oxygen has not, when pure, been solidified, but liquid air is readily brought to the solid state by rapid evaporation under reduced pressure (Dewar, Proc. Roy. Inst., 19 Jan. 1894). Whether the solid in this case is homogeneous or only a magma of solid nitrogen mixed with liquid oxygen might be questioned*, but at all events it must contain oxygen at the lowest temperature that can practically be reached. We therefore tried whether we could detect any difference between the absorptions of solid and liquid air. There was no difference that we could detect in the character of the absorptions, and not much in their intensities.

In order to test further the effect of temperature, we compared the absorption of a thickness of 3 centim. of liquid oxygen boiling under about 1 centim. pressure with that of a like thickness of the liquid boiling at atmospheric pressure. With the colder liquid the bands in the orange and yellow were sensibly widened, mainly on the more refrangible side, the faint band in the green was plainly darker, and the band in the blue appeared somewhat stronger. The difference between the temperatures of the two liquids may have been about 17° C., which does not appear to be a great difference; but then it is nearly one fifth of the absolute temperature of the warmer liquid. The increased density of oxygen at −200° C., according to Janssen's law, if extended to the liquid state, should make the absorption greater by about 20 per cent. as compared with that at its boiling-point.

XXII. *On the Critical Temperature of Hydrogen and the Theory of Adiabatic Expansion in the Neighbourhood of the Critical Point.* By Dr. LADISLAS NATANSON, *Professor of Natural Philosophy in the University of Cracow†.*

I.

LET us consider a set of "ideal" gaseous bodies; the fundamental assumption we shall adopt is that not

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* I have observed that solid air when placed in a strong magnetic field has the oxygen sucked out of it towards the poles, so that there seems little doubt that the solid air is only a magma of solid nitrogen mixed with liquid oxygen.—J. D.

† Abstracted from the *Bulletin International de l'Académie des Sciences de Cracovie,* Mars et Avril 1895. Communicated by Prof. Olszewski.

only the ideal gaseous laws usually so called, but likewise the well-known general Law of Thermodynamic Correspondence are to a sufficient degree of approximation obeyed by them. Thus, with M to denote the molecular weight, and C a constant, of the same value for all bodies,

$$pv = \frac{C}{M}t ; \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

and if the p, v, t of every gas be expressed as multiples of their critical values p_c, v_c, and t^c; that is, if we write

$$\pi = \frac{p}{p_c}, \quad \omega = \frac{v}{v}, \quad \text{and } \tau = \frac{t}{t_c}, \quad \text{then}$$

$$\pi\omega = K\tau ; \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where K is another universal constant. From these equations it follows at once that

$$t_c = AMp_c v_c, \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where again A is a constant quantity, the value of which is the same for all bodies. Now M. Amagat finds for carbonic acid,

$$t_c = 273 + 31\cdot35 ; \quad p_c = 72\cdot9 \text{ atm. } ; \quad \frac{1}{v_c} = 0\cdot464 \frac{\text{gm.}}{\text{cm.}^3} ;$$

hence, taking one gramme as unit molecular weight and one dyne per cm.² as unit pressure, we obtain

$$A = 0\cdot4344 . 10^{-7} \left(\frac{\text{abs. degree}}{\text{erg}} \right).$$

The following table shows values of A calculated for several gases :—

Substance.	M.	t_c	A.
Carbonic Acid, CO_2.........	44	304·35	$0\cdot4344 . 10^{-7}$
Ethylene, C_2H_4..............	28	283	$0\cdot424 . 10^{-7}$
Sulphurous Acid, SO_2	64	429	$0\cdot436 . 10^{-7}$
Nitrous Oxide, N_2O.	44	309·4	$0\cdot389 . 10^{-7}$
Sulphuric Ether, $C_4H_{10}O$...	74	467·4	$0\cdot430 . 10^{-7}$
Nitrogen, N_2	28	127	$0\cdot47 . 10^{-7}$

It will be observed that the differences between the values of A do not appear to be in any connexion whatever with the M's or t_c's ; and, since the accuracy of the experimental data

is by no means satisfactory, we shall in the following calculation take the value of A deduced for carbonic acid as that which is probably nearest the truth [*].

Could the critical volume of hydrogen be evaluated, equation (3) shows us that the unknown value of the critical temperature of hydrogen would follow at once. In order, then, to estimate the critical volume, observe that between limits from 100 to about 600 atm. hydrogen sensibly obeys "Bernoulli's Law," that is, the relation

$$p(v-b) = \mathrm{R}t, \quad \cdots \quad \cdots \quad (4)$$

b being a constant quantity. (Of course equation (4) is only an approximation, because otherwise a critical state would be altogether impossible.) But then M. van der Waals' equation

$$\left(p + \frac{a}{v^2}\right)(v-b) = \mathrm{R}t \quad \cdots \quad \cdots \quad (5)$$

may be said to be applicable with due approximation as well, if we agree to select for the constant a some value which sufficiently approaches zero. From (5) we obtain

$$v_c = 3b \ldots (\alpha); \quad p_c = \frac{a}{27b^2} \ldots (\beta); \quad t_c = \frac{8a}{27b\mathrm{R}} \ldots (\gamma); \quad (6)$$

and

$$\frac{t_c}{p_c} = \frac{8b}{\mathrm{R}}. \quad \cdots \quad \cdots \quad \cdots \quad (7)$$

For hydrogen the constant a cannot be evaluated; in the particular case of hydrogen, therefore, equations (6β) and (6γ) are of no use; equations $(6a)$ and (7), on the contrary, being independent of the value of a, may be taken to hold, even if $a = 0$. Thus it is seen that a fairly approximate value of the critical volume of hydrogen is to be found in $3b$. From the compressibility experiments published by M. Amagat in 1881, the value of b for hydrogen has been found by Prof. Witkowski to be ·00067 for pressures ranging from 30 to 300 metres of mercury, the unit volume being that occupied by the gas at zero Centigrade and one atmosphere pressure; and from M. Amagat's later investigation, which he published in 1893, I myself deduced (for zero Centigrade and pressures between 150 and 550 atm.) values included between ·00070 and ·00074. Assuming, then, $b = $ ·00070, we find the critical

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[*] In his celebrated Thesis, M. van der Waals has given an equation which, although in a somewhat particular form, nearly coincides with the above (3). Prof. Sydney Young and M. Guye have given much attention to its verification, and the values of A thus obtained would differ but little from that here adopted.

volume of hydrogen to be $23 \cdot 45 \frac{\text{cm.}^3}{\text{g.}}$ and the critical density

to be $\cdot 043 \frac{\text{g.}}{\text{cm.}^3}$. If these values be adopted as well as that

of p_c, supposed by Prof. Olszewski to be equal to 20 atm. (see below), then equation (3) gives

$$t_c = 41 \cdot 3, \; i. \, e. \text{ approximately} -232° ;$$

therefore the Law of Thermodynamic Correspondence requires us to expect the critical temperature of hydrogen to be situated in the proximity of $-232°$, the limits which the uncertainty in the values of b allows for being $-229°$ and $-234°$ C. respectively.

If we assume $-232°$ to be the critical temperature and 20 atm. to be the critical pressure of hydrogen, we may calculate the boiling-point as follows. At that point the " specific" value of the saturation pressure will be $\frac{1}{20}$ or $\cdot 05$; and the corresponding " specific" value of the absolute temperature is (for all bodies) $\cdot 706$. Hence the boiling-point of hydrogen will be $-244°$. Diminishing the pressure, the following temperatures would be reached :—

At 608 millim.	$-244 \cdot 5$	At 60·8 millim.	$-249 \cdot 3$
„ 456 „	$-245 \cdot 3$	„ 30·4 „	$-250 \cdot 4$
„ 304 „	$-246 \cdot 3$	„ 15·2 „	$-251 \cdot 4$
„ 152 „	$-247 \cdot 7$	„ 7·6 „	$-252 \cdot 3$
„ 121·6 „	$-248 \cdot 1$	„ 3·8 „	$-253 \cdot 2$
„ 91·2 „	$-248 \cdot 6$	„ 1·5 „	$-254 \cdot 2$

Professor Olszewski has explained in the Philosophical Magazine (for February 1895, pp. 202–203) how the experiments he describes led him to the conclusion that the critical pressure of hydrogen is 20 atm. Let us translate Prof. Olszewski's reasoning into symbols. If we suppose for a moment that the expansion (assumed to be adiabatic) which begins with certain special values p_0 and t_0 of the pressure and temperature, is just what is needed to carry the gas down simultaneously to the critical temperature t_c and the critical pressure p_c, then, to a first approximation,

$$\left(\frac{t_c}{p_0}\right) = \left(\frac{p_c}{p_0}\right)^{k-1} \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (8)$$

(where the well-known ratio of specific heats, or about 1·4 for hydrogen, is denoted by k). Substituting in (8) the data

quoted by Prof. Olszewski, viz.:—

$$t_0 = 273 - 211 = 62 \; ; \quad p_c = 20 \text{ atm.} \; ; \quad p_0 = 80 \text{ atm.} \; ;$$

we find $\qquad t_c = 41 \cdot 7 \; ; \quad i. e. \text{ about } -231°.$

Now, in order to evaluate the error which the omission of the absorption of heat may have introduced, it must be borne in mind, first, that the phenomenon of expansion lasted but one second or two, according to the information with which Prof. Olszewski has favoured us ; and, secondly, that the circumambient temperature was $-211°$. Moreover, the critical temperature of oxygen may be calculated in the same way. With the data

$$t_0 = 170 \cdot 5, \quad p_c = 51 \text{ atm.}, \quad p_0 = 80 \text{ atm.},$$

which are given by Prof. Olszewski, equation (8) yields the result $-123°$ for the critical temperature of oxygen, which is known to be situated at $-118° \cdot 8$. We should assume, accordingly, that the critical temperature of hydrogen lies at some few degrees above $-231°$, at $-228°$ for instance.

II.

The theory of adiabatic expansion in a system consisting of a liquid and of saturated vapour was originated by Clausius and Rankine, verified by Hirn and Cazin, and has been recently developed by M. Duhem [*] and M. Raveau[†]. In the following pages it will be our object to apply this theory to problems suggested by Prof. Olszewski's beautiful experiments on hydrogen.

Let m, w, σ denote the mass, the volume, and the entropy per unit mass for the liquid ; and M, W, Σ the same quantities when referring to the vapour ; let V be the total volume, and S the total entropy of the system, T its absolute temperature, assumed to be uniform throughout, p the general value of the pressure, and P the saturation pressure corresponding to T. If we write for brevity's sake

$$\frac{\partial}{\partial T} + \frac{dP}{dT} \frac{\partial}{\partial p} = \frac{d}{dT} \text{ say,} \quad \cdots \quad (1)$$

then

$$dV = (W - w)dM + \left(m \frac{dw}{dT} + M \frac{dW}{dT} \right) dT, \quad \cdots \quad (2)$$

$$dQ = T(\Sigma - \sigma)dM + T\left(m \frac{d\sigma}{dT} + M \frac{d\Sigma}{dT} \right) dT \; ; \quad \cdots \quad (3)$$

[*] *Travaux et Mémoires des Facultés de Lille*, t. i. no. 5, p. 83, *Journal de Physique*, [3] i. p. 470.
[†] *Journal de Physique*, [3] i. p. 461.

here $d\mathrm{Q}$ is the quantity of heat absorbed in an elementary reversible transformation. Put

$$\mathrm{T}\frac{d\sigma}{d\mathrm{T}}=\gamma\,;\quad \mathrm{T}\frac{d\Sigma}{d\mathrm{T}}=\Gamma\,;\quad\ldots\quad\ldots\quad(4)$$

γ and Γ will be what is termed *the specific heat of saturated liquid* and *of saturated vapour* respectively. Lastly, if L stands for the heat of vaporization per unit mass, consider the quantity

$$\mathrm{A}=\frac{(m+\mathrm{M})\gamma}{(m\gamma+\mathrm{M}\Gamma)(\mathrm{W}-w)-\mathrm{L}\left(m\dfrac{dw}{d\mathrm{T}}+\mathrm{M}\dfrac{d\mathrm{W}}{d\mathrm{T}}\right)}\quad.\quad.\quad(5)$$

If certain assumptions be conceded (which have been advanced by M. Raveau with respect to the specific heats at constant volume), it may easily be proved, as M. Duhem has shown, that A will be positive at every temperature. Taking this for granted, consider the case of adiabatic expansion, so that $d\mathrm{V}>0$ and $d\mathrm{Q}=0$. From (2), (3), and (5) we obtain

$$\left(\frac{d\mathrm{M}}{d\mathrm{V}}\right)_{\mathrm{s}}=\mathrm{A}\left(1-\frac{l}{\lambda}\right),\quad\ldots\quad\ldots\quad(6)$$

the symbols l and λ being defined as follows :—

$$l=\frac{\mathrm{M}}{m+\mathrm{M}}\,;\quad \lambda=\frac{\gamma}{\gamma-\Gamma}\,;\quad\ldots\quad\ldots\quad(7)$$

here λ is some definite function of the absolute temperature, and l may be termed *the degree of evaporation*. We propose to call those curves on the p V-diagram which correspond to given constant values of l *isopsychric lines*. Equation (6) shows that the isopsychric line $l=\lambda$ is at every temperature a tangent to the adiabatic line ; and from the same equation the relative positions of other isopsychrics and adiabatics, in the neighbourhood of the points of their mutual intersection, may be inferred. The general nature of the relation between γ, Γ and therefore λ and the temperature is pretty well known : thus at low temperatures λ rises from very small values, possibly from zero, becomes equal to unity at *the first point of inversion*, which we shall denote by T*; then as the temperature increases, λ still increases and attains a *maximum* λ_m ; then it begins to decrease, becomes again equal to unity at *the second point of inversion* T**; lastly, it further decreases and at the critical point becomes probably equal to $\frac{1}{2}$, since (as shown by M. Raveau) the ratio γ/Γ tends there to become equal to -1. In fig. 1 the saturation line AcB is shown, as well as a set of *real* isopsychrics corresponding to values of l inferior to unity, further *imaginary* isopsychrics corresponding to values

of l superior to unity (of which one only, $l=\lambda_m$, is given), and lastly the "neutral line" c N, *i. e.* the curve passing through

Fig. 1.
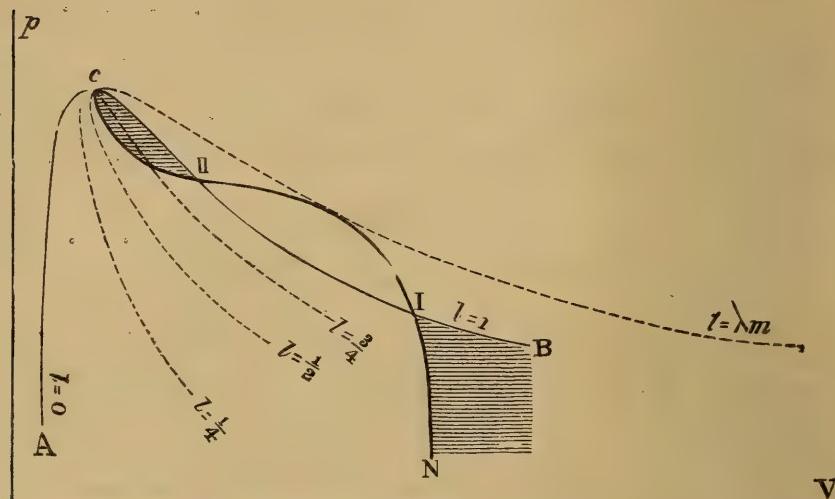
the points of contact between adiabatics and isopsychrics. The points I and II correspond to the inversion points T^* and T^{**} respectively. In portions of the plane situated to the right of the neutral line, expansion ought to be accompanied by condensation; in those situated to the left it ought to be accompanied by evaporation; but since for the masses of liquid and vapour negative values cannot be realized, condensation for instance will occur within the limits of the shadowed areas only.

Let us now consider a gas at a temperature T_0 which we suppose to be above the critical temperature. If the gas be submitted to adiabatic expansion, the path of the representative point in the pV-plane will be an adiabatic curve which will begin on the T_0-isothermal line. Let us suppose that R_a, R_b, R_c, R_d ... represent the pressures, and S_a, S_b, S_c, S_d ... the entropies of the gas (per unit mass) at the points of issue of the adiabatics; and let Q_a, Q_b, Q_c, Q_d ... denote the pressures, and T_a, T_b, T_c, T_d ... the temperatures at the places where they intersect the line of saturation, Q_c and T_c being the critical values. We shall have

$$\sigma(Q_a, T_a)=S_a; \quad \sigma(Q_b, T_b)=S_b,$$
$$\sigma(Q_c, T_c)=\Sigma(Q_c, T_c)=S_c, \quad \left.\begin{array}{c} \\ \\ \\ \end{array}\right\} \quad . \quad . \quad . \quad . \quad . \quad (8)$$
$$\Sigma(Q_d, T_d)=S_d, \text{ \&c., \&c.}$$

Considering two infinitely near adiabatics :—

$$\delta S = \left(\frac{dS}{dT}\right)\delta T = \frac{G}{T}\delta T \text{ and } \delta Q=\left(\frac{dP}{dT}\right)\delta T, \quad . \quad . \quad (9)$$

in which G stands either for γ or Γ according as the point of intersection with the line of saturation lies on the fluid or on the vapour branch. If now we suppose the "ideal" gaseous laws to express the behaviour of the body at the temperature T_0 with sufficient approximation * we may put

$$S = C \log T_0 - c \log R + S_0 \text{ and } \delta S = -c \frac{\delta R}{R}, \quad . \quad (10)$$

where C, c, and S_0 are constant quantities; hence

$$\frac{\delta Q}{\delta R} = -\frac{c T \frac{dP}{dT}}{RG}, \quad . \quad . \quad . \quad . \quad . \quad (11)$$

and thus the value of $\delta Q/\delta R$ at the critical point is seen to be zero. Let R_c be the initial pressure, on the T_0-isothermal line, which belongs to the "critical" adiabatic, *i. e.* to the adiabatic crossing the line of saturation at the critical point. Adiabatic curves with initial pressures R_1 *superior* to R_c will then be found to intersect the line of saturation on the liquid side and at pressures Q_1 satisfying the relation

$$\frac{\delta Q_1}{\delta R_1} = -\frac{c T_1 \left(\frac{dP}{dT}\right)_1}{R_1 \gamma}; \quad . \quad . \quad . \quad . \quad (12)$$

consequently the pressures Q_1 will decrease when the R_1's increase. At the pressure Q_1, therefore, when following the course of an adiabatic, we should observe the appearance of the *first bubbles of vapour*; and above Q_1 it will only be the homogeneousness of the system which will prevent our ascertaining its *liquidity*. On the other hand, adiabatic curves whose initial pressures R_2 are inferior to R_c will intersect the line of saturation on the vapour side, at pressures Q_2 such that

$$\frac{\delta Q_2}{\delta R_2} = -\frac{c T_2 \left(\frac{dP}{dT}\right)_2}{R_2 \Gamma}, \quad . \quad . \quad . \quad . \quad (13)$$

so that (between the critical temperature and the temperature T^{**}) the pressures Q_2 decrease when the R_2's decrease.

Let us now proceed to consider the variations of the pressures Q_1 on the left, and those of the Q_2 on the right of the critical point. We may put $\delta R_1 = \delta R_2$; this, in fact, is what Prof. Olszewski directly realized. If we compare such

* That for Prof. Olszewski's experiments such an assumption is legitimate, may be seen from the following argument. The temperature T_0 in these experiments was $-211°$, *i. e.* 62 degrees on the absolute scale. The critical temperature of hydrogen lies about $-232°$. Hydrogen at $-211°$ may therefore be compared with carbonic acid if taken at $+187°$.

variations δQ_1 and δQ_2, as correspond to equal temperatures $T_1 = T_2$, we obtain

$$\frac{\delta Q_1}{\delta Q_2} = \frac{R_2 \Gamma}{R_1 \gamma}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

and from this it appears that at the critical temperature the value of the ratio $\delta Q_1/\delta Q_2$ is equal to -1, but that at lower temperatures it rapidly decreases and becomes zero at the second point of inversion T^{**}: thus in the neighbourhood of the temperature T^{**} the differences δQ_2 must infinitely surpass in value the correlated differences δQ_1. This result furnishes us, I think, with a satisfactory thermodynamical explanation of the phenomena which Prof. Olszewski observed when he submitted to adiabatic expansion hydrogen cooled to $-211°$. The pressure he evaluates to be about 80 atm. is evidently what we have called R_c; and 20 atm. indeed is the critical pressure δ_c or Q_c. In order to obtain a numerical illustration, let us assume that the intersection points of the two adiabatics $R_1 = 90$ atm. and $R_2 = 70$ atm. with the line of saturation are comparable with one another; further on Γ/γ to be equal, say, to $-·05$ at the temperature of intersection. Then, δQ_2 being 2 atm., we obtain $\delta Q_1 = -·078$ atm., and this, as Prof. Olszewski has been kind enough to inform us, is much below the minimum change accessible to observation.

Another point of interest is the following. From what has been said above, it will be seen that at the second point of inversion T^{**} (or II in fig. 1) the adiabatic curve is tangent to the line of saturation, and therefore does not penetrate into the domain of vapour and liquid coexistence of which that line constitutes the boundary. Adiabatics then, which begin with smaller initial pressures than the particular adiabatic referred to, will be situated in the domain of superheated vapour; it is only at a temperature below the first point of inversion T^* and at a pressure K inferior to P* that such an adiabatic may enter the "domain of coexistence." And again, such adiabatics as begin with greater initial pressures than the particular adiabatic referred to must twice intersect the line of saturation; the first time at a pressure Q while entering the domain of coexistence, and the second time at another pressure H while leaving it. Now let us suppose adiabatic expansion to be effected along such an adiabatic curve; something like a fog or a cloud will obviously appear at Q and again disappear at H. (The pressures Q will increase, and those denoted by H will decrease if the initial pressures R are increasing; and the two saturation pressures P* and P** will be the limits between which the

pressures H must be included, see fig. 2.) By these considerations the nature of the phenomenon which Prof. Olszewski described as *sudden ebullition* may, perhaps, be

Fig. 2.
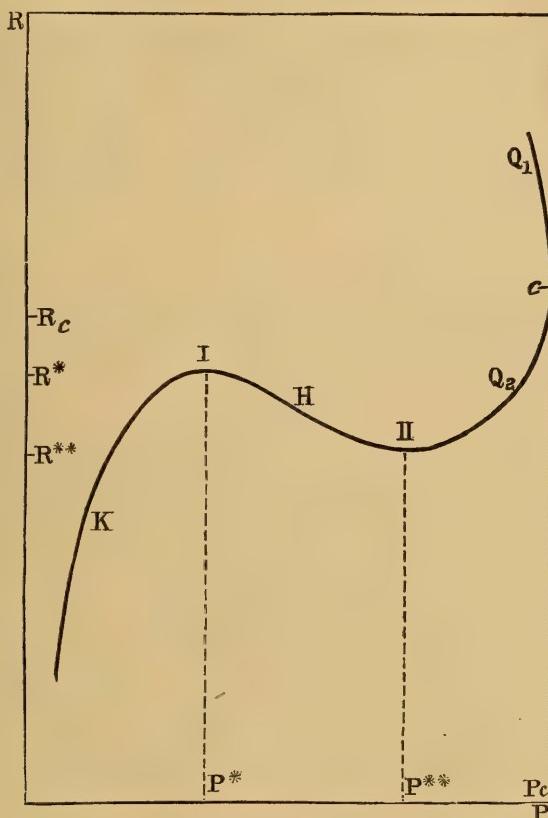
thermodynamically explained. He observed the liquefied droplets disappear again rapidly as soon as formed ; this, it seems to us, may be directly the effect of the expansion itself, if the pressure H is reached soon after Q is reached. Thus the values 18 and 16 atm. quoted by Prof. Olszewski may possibly represent some intermediate pressures between the corresponding Q and H ; and if such be the case, still easier will it be to explain why these values decrease rapidly below the critical point.

The last question we propose to examine is, Can the situation of the points of inversion be evaluated for hydrogen? Since with regard to this no source of information of any trustworthiness whatever seems to be open to us, we venture, with much diffidence, to advance the supposition that the points of inversion may be thermodynamically correspondent temperatures ; that is, if we define τ^* to mean T^*/T_c, and τ^{**} likewise to mean T^{**}/T_c, that for different bodies the values

of the τ^*, and those, on the other hand, of the τ^{**}, may possibly be identical. In fact, it is found that the values of τ^* are practically identical for benzene, chloroform, and carbon tetrachloride, being equal to about ·70. For water, aceton, and carbon bisulphide τ^* seems to be somewhat higher, whereas for ether it is much lower : such results, however, do not seem to deserve much confidence. Still, if we assume for a moment τ^* for hydrogen to be ·75 say, we find $-242°$ for T* ; and then the second point of inversion ought to lie somewhere between that temperature and the critical, that is, $-232°$.

XXIII. *The Measurement of Cyclically Varying Temperature. By* Henry F. W. Burstall, *M.A., A.M.I.C.E.**

[Plates I. & II.]

I HAVE been engaged since the latter end of 1892 in attempting the measurement of the temperatures reached in the cylinder of a gas-engine, and the following paper embodies the results which I have obtained.

So far as I am aware no experiments on this subject have been previously published; such attempts as have been made have failed from the want of a sufficiently sensitive thermometer. The platinum resistance-thermometer has, however, proved to have the required sensitiveness, and I shall devote this paper to the description of one of its forms which I have found suitable for the measurement of cyclically varying temperature.

The direct determination of the temperature in the cylinder clears the field for more complete discussion of the theory of the gas-engine, but as I would rather treat the experiments which I have already made as preliminary only, I will not enter into any discussion on this point in the present paper.

I had hoped during this work to have had the collaboration of Prof. Kapper, but unfortunately, owing to the pressure of other work, he was unable to devote the necessary time to these researches. I wish to take this opportunity of thanking him for putting at my disposal the experimental gas-engine at King's College, and also for many valuable suggestions he has made during the course of the work.

The engine used is an Otto cycle-engine. This cycle, which is that now most generally used in internal combustion-engines, is completed in four strokes of the piston.

During the first stroke a charge of mixed air and combustible gas is drawn into the cylinder by the forward motion of the piston, the air- and gas-valves are now closed automatically, and the piston, on its second stroke, compresses the mixture, nearly adiabatically *, into the clearance space. This space forms a prolongation of the working cylinder, and has a capacity of about 45 per cent. of the volume swept through by the piston. The pressure reached at the end of the compression strcke is thus about four atmospheres. At the commencement of the third stroke communication is opened to the ignition-tube; the mixture then explodes, and the pressure rises to about fifteen atmospheres. The piston moves forward and the pressure falls, as the heated gases expand, until it is about three and a half atmospheres. This takes place just before the end of the stroke, and at this point the exhaust-valve opens. During the fourth stroke the products are discharged from the cylinder.

In order to measure the extremely high temperatures which were known certainly to be reached during such a cycle, some special form of thermometer had to be employed : not only is the temperature high, but the pressures to be dealt with are such as to destroy any thermometer not constructed of materials capable of resisting great mechanical stresses. It appeared to me that the platinum resistance-thermometer, which has been brought to such perfection by Callendar and Griffiths, and whose constants can be determined with such a high degree of accuracy, gave the greatest promise of success.

The general form and construction of such thermometers are now so well known, that I will only describe the special form which I have employed to fulfil the following conditions, which had to be satisfied in this particular case :—

(i.) The thermal capacity must be small, as the variations of temperature are extremely rapid. A whole stroke of this engine is completed in less than one fourth of a second; during this time the temperature varies about 500° C., and as the temperature has to be measured at any fraction of the stroke, a lag of 0·01 second corresponds to one tenth of the stroke of the piston.

(ii.) The body of the thermometer must be made of some strong material such as iron or steel, as the impulsive pressures would immediately destroy any weaker material.

* During compression the pressure and volume are approximately connected by the relation $pv^{1\cdot3} = \text{constant}$.

(iii.) From the nature of the thermometer chosen, the
leads must be well insulated from each other and from
the body of the instrument, the insulating material
being such as to stand high temperatures.

To fulfil all these conditions was by no means easy. In
order to satisfy the first I was forced to employ a naked wire
of small diameter, which obviously gives the minimum ther-
mal capacity per unit of surface. I was fully aware that the
whole of Callendar and Griffiths's work had been done on wires
which were carefully shielded from the least contamination by
means of an outer envelope; hence it might have been expected
that a naked wire would prove unreliable, but I show later
that, provided suitable precautions are taken, naked wires give
satisfactory results, at any rate to the order of accuracy of my
experiments.

The difficulties of obtaining the requisite mechanical
strength, and at the same time good insulation, were very
great; and nearly twelve months' work was expended
before a satisfactory solution of the problem was obtained.
The greater number of the earlier instruments were deficient
in mechanical strength. In most laboratory experiments this
is seldom of great importance; but this weakness invariably
led to the thermometer being blown out of the engine after
a few explosions, and the results were disastrous to the
experiments.

Description of the Thermometer.   (Plate I. fig. 1.)

The body of the thermometer consists of a seamless steel
tube 15 inches long and ¾ inch outside diameter; the outside
of the tube is screwed from end to end with a fine thread.
Working on this thread is a nut N, so arranged that the
thermometer-wire can be immersed to any required depth in
the gas-engine cylinder. For a distance of about one inch
from one end, A, the tube is threaded in the interior and
a small ring screwed in. Against this ring, which forms an
internal collar, rests a circular slate block (C) pierced with
four small holes through which the four leads pass. These
leads are of platinum, 0·03 inch diameter and 4 inches long.
About 1·5 inches from the end A small platinum collars are
gold-soldered on to the leads; these prevent the leads from
being blown out of the tube, by bearing against the slate
block. In the stem of the thermometer the leads are of stout
copper soldered with brass to the platinum leads and separated
from each other by mica washers. After the leads have been
put in position, a packing of alternate layers of asbestos and
mica washers is placed on the slate block, as shown in the

figure, and by means of the screw-gland D is forced into all the interstices—the instrument thus being made tight under the pressure. Four leads are used, two being joined by the measuring-wire, the other two being joined directly together*.

Description of the Resistance-Measuring Apparatus.

In order to readily eliminate the changes of resistance of the leads, an equal-arm slide-bridge was employed. The connexions are shown diagrammatically in fig. 2.

In the arm A are placed the main leads ; in the opposite arm B are the compensating leads in series with the resistance-box. In the arms C and D are two carefully adjusted equal coils, each having a resistance of about 8 ohms. The bridge-wire is of platinum-iridium, and is half a metre long ; its resistance is 0·2980 ohm at 15° C. This wire was calibrated by Carey Foster's method, and, for the degree of accuracy required (0·001 ohm), was found to be of sensibly equal resistance per unit length throughout.

The galvanometer, a very dead-beat astatic instrument, had a resistance of about 100 ohms. The magnet system and mirror were suspended by a quartz fibre 1·5 inches long, and was damped by a specially large mica damper very closely enclosed.

The scale was placed 4 feet from the mirror, so that a change of resistance of 0·0005 ohm could be readily detected.

The resistance-box was an ordinary plug series box with platinoid coils. It was, in the first instance, calibrated by Mr. E. Wilson, of King's College ; but after considerable use so much trouble was given and, indeed, so many experiments spoiled through the inefficiency of the plugs, that links, screwed up by a screwdriver, were substituted for them. Although the links are not so convenient to work with as the plugs, the results have been in every way satisfactory since this change. I then re-calibrated the box, and the two determinations were in fair agreement. Below I give a table of the values of the coils used during the experiments :—

Nominal value of coil. ohms.	Calibrated value at 11° C. ohms.	
0·5	0·5063	
1	1·0042	
2	2·0020	In terms of my coil,
2	2·004	C.L.C. 417.
5	5·013	

* For permission to use the compensators (the invention of Mr. Callendar), I am indebted to the Cambridge Scientific Instrument Company.

As the working stroke in the Otto cycle only occurs once in four strokes of the piston, and as the temperature had to be measured at particular parts of that stroke, it was necessary that the galvanometer should only be in circuit at the right moment, otherwise the galvanometer swing would not give an indication of the true temperature of the wire. During each explosion stroke the measuring-wire goes through the whole cycle of temperature and, in order to secure a particular epoch of this stroke, the following arrangement of contact makers (shown in fig. 3) was designed. The galvanometer circuit was broken in two places, one of which was made during every working stroke, and the other at a definite epoch at every revolution; thus the galvanometer circuit was only completely made at one definite point in every working stroke. At any required point in the stroke of the piston, contact is made every revolution by a cam (C) on the crankshaft of the engine lifting one end of a vibrating lever, depressing a wire (B), fixed to the other end, into a mercury cup D, and thus making a galvanometer contact for a definite time (about $\frac{1}{20}$ of the stroke) at a certain fraction of the stroke. This, however, makes contact once every revolution, while the temperature is measured only during an explosion stroke. To ensure that the galvanometer circuit shall only be made during every working stroke, it is again broken and only made at the proper time by a relay. This relay is on a separate circuit which is completed by means of a steam-engine indicator (P), whose pencil is replaced by a metal point. During the compression and exhaust strokes the pencil bears on a boxwood cylinder, but when the explosion occurs the arm is forced upwards by the pressure and the pointer makes contact on a strip of brass Q, thus completing the relay circuit. The electromagnet is excited and the beam depressed, completing the galvanometer circuit through the mercury cups R and S. As soon as the relay has moved through a small distance, the indicator break is short-circuited by the mercury cup T, and thus the relay circuit remains closed until broken by a contact on the exhaust-valve of the engine. Although somewhat complicated this relay was found to work well, but great care had to be taken that the contacts were all well amalgamated and the mercury clean, otherwise the very small currents in the galvanometer circuit, when a balance is nearly obtained, are entirely broken by any dirt or grease.

To make a determination of the temperature at any required point the contact-maker on the engine-shaft was set, by means of marks on the driving pulley, to make contact at the required position of the piston. An approximate

balance was then found by putting a suitable resistance in the box and adjusting the position of the slider on the wire. If the temperature had been the same at the same point in the stroke in every working stroke, an accurate balance could have been obtained by shifting the slider till the deflexion of the galvanometer was reduced to zero, but this, however, was not the case, and no attempt in the later work was made to obtain an accurate balance on the bridge-wire. The slider was set in such a position that the galvanometer threw about six scale-divisions to one side of zero, and ten successive throws observed. The slider was then moved until the galvanometer threw about six divisions on the other side, and ten throws observed. By taking the mean of these and interpolating, the true reading on the bridge-wire was obtained.

The gas-pressure was rising towards the end of the experiment from 1·6 to 1·9 inches of water.

Below I give a specimen page of my note-book :—

<div align="center">

Resistance in box 2·2 ohms.

Bridge-wire.

</div>

Galvanometer-throws at	500	200	300
	6 left	3 right	2 right
	5	14	0
	7	5	10
	8	16	3
	7	7	7
	3	15	12
	4	24	5
	10	10	16
	4	15	17
	6	25	3
Mean	6·0 left	13·4 right	7·5 right

Taking the throws at 500 and 300 we obtain, by interpolation from the throws, a bridge-wire reading of 407, and taking those at 500 and 300 we obtain a reading of 411.

One division on the galvanometer-scale corresponds to from 15 to 50 divisions of the bridge-wire scale, the former figure being for points towards the end of the stroke, and the latter for points towards the commencement of the stroke of the engine. As a check on this method, I have taken the bridge-wire reading from three points or more instead of two, and have found the results obtained agreed within a few scale-divisions of the bridge-wire. To be accurate, this method presupposes constancy in the testing battery, and in the earlier work considerable trouble was found from the variation of the battery, which was two Leclanché cells. In the later work, both in the determination of the fixed points of the thermometers and for the experiments in the gas-engine, a single Daniell cell with an added resistance of

about 20 ohms was used, and even after many hours' work was found perfectly constant.

There now remains the question, when the resistance of the measuring-wire at any point has been determined, what temperature on the air-scale corresponds to the resistance found. Callendar has shown that if temperature, in degrees Centigrade, be denoted by t, and pt denotes what is called the platinum temperature, then

$$t - pt = \delta \left(\frac{t^2}{100^2} - \frac{t}{100} \right),$$

where δ is a constant which has to be determined for any particular platinum wire; pt is defined as equal to

$$100 \frac{R - R_0}{R_1 - R_0},$$

where R_0 is the resistance of the wire in melting ice, R_1 is the resistance of the wire in steam at atmospheric pressure, and R the resistance of the wire at the temperature t [*].

As my thermometers consisted of very fine naked wires which were, of necessity, exposed to the erosive action of high-temperature gases, it could not be expected that the fixed points, *i. e.* the resistance in ice and steam, would remain constant after the wire had been in the cylinder for any length of time. Also, owing to the irregular working of the gas- and air-valves, the temperatures reached in the cylinder sometimes far exceeded the mean. When one of these abnormal explosions occurred the wire was sometimes completely fused, and more frequently melted on the surface. These two causes necessitated a frequent determination of the fixed points and also of the value of δ.

Three sizes of measuring-wire were used : they were all about $\frac{3}{4}$ inch long, their diameters being 0·003, 0·0025, and 0·002 inch respectively. The weights of these wires are approximately 0·00182, 0·0013, and 0·00081 gramme respectively, whence, taking the specific heat of platinum as 0·037, the thermal capacities are 0·0000673, 0·0000481, and 0·00003 gramme-degrees respectively.

I had intended to measure the temperatures by means of all three wires, and from the results obtain a curve giving the lag of the wires; this was, however, not possible owing to want of time and apparatus, but the two finer wires gave temperatures which were nearly equal, while the coarser wire gave results somewhat lower than the two others. This induced me to work with the 0·0025 wire for the bulk of the experiments, as the 0·002 wire had so little mechanical

* Phil. Trans. A, 1887.

strength that, if an abnormal explosion occurred, it was invariably destroyed.

Calibration of the Thermometers.

The ice points call for no special remark beyond the fact that, in spite of considerable care in ensuring a mixture of finely crushed ice and water, they were by no means as satisfactory as the steam points. The average resistance of the 0·003, 0·0025, and 0·002 inch diameter wires was 0·3, 0·55, and 0·75 ohm respectively. The steam points were obtained in a double-jacketed hypsometer of the ordinary form, and were corrected for barometric pressure when necessary. When working with these very fine wires, it is imperative to guard against the heating effect of the battery current, otherwise discrepant and inaccurate results are obtained. I have found that the Daniell cell, mentioned above, with resistance in the external circuit gave no appreciable heating unless the observations were made too rapidly. (This of course only applies to the ice and steam points; when in the engine battery heating is of no importance.)

Two methods were used to obtain the quantity δ. The first method was a comparison of the fine-wire thermometer with a standard Callendar platinum thermometer, both being placed in a tube heated to a high temperature, thus getting a third point on the curve connecting the air and platinum scales.

The standard thermometer consisted of a spiral of platinum wire of a diameter of 0·008 inch wound on a flat plate of mica and enclosed in a porcelain tube 50 centimetres in length, the flat spiral occupying a length of about 7 centimetres from the closed end of the platinum tube. The fixed points of this thermometer were determined many times in ice and steam, and several times in sulphur and aniline vapours. The values were

$$R_0 = 2 \cdot 936 \text{ ohms,}$$
$$R_1 = 4 \cdot 080 \text{ ohms,}$$
$$\delta = 1 \cdot 52.$$

I have not been able to detect any change in the zero, although this thermometer has been raised to a bright red heat several hundred times during the last two years.

For the comparison of the two thermometers an ordinary gas-furnace, such as is used for combustion work, was first used, but was abandoned owing to unequal and unsteady heating. After some trials I adopted a tube-furnace heated with gas-coke; from end to end of the furnace (about 2 feet in length) was placed a cast-iron tube $2\frac{1}{2}$ inches diameter

outside and $\frac{1}{2}$ inch thick. This tube could be rotated in bearings, and thus the temperature could be kept steady round the circumference. Inside the cast-iron tube, and independently supported, was a thick copper tube in which were placed the two thermometers for comparison, the fine wire of the steel-tube thermometer nearly touching the porcelain tube of the standard. Owing to the great mass of the metal, the temperature in the inner tube changed very slowly, and by regulating the draught a temperature of 500° to 600° C. could easily be obtained. Although this was much better than the gas-furnace, as regards an equal temperature circumferentially, still it could not be assumed that the whole length of the coil of the standard thermometer was at the same temperature as the fine wire on the steel-tube thermometer. During any comparison the standard did not show a variation of more than 2° C. Unfortunately the fine wire having such a small thermal capacity as compared with the standard, may not be at quite the same temperature as the standard if there is even the slightest change in the temperature. For these reasons the values of δ as determined by this method are not so satisfactory as might be wished.

In the second method the resistance of the steel-tube thermometer was determined in sulphur vapour as well as in ice and steam. The sulphur was boiled in an apparatus similar to the first form used by Callendar and Griffiths in their determination of the boiling-point of sulphur [*]. This consisted of a boiler and condenser made of iron tubes. While this method gives very accurate and satisfactory results, it requires extreme care and takes several hours to obtain a steady temperature.

Results of the Experiments.

It was not until the summer of 1894 that I was able to make any proper experiments with the wires in the cylinder of the gas-engine. I directed my attention at first to the determination of the best speed for the engine, and to find what conditions were necessary to obtain regularity and to ensure that the measuring-wire should follow the temperature of the expanding gases. I found that to obtain regular and perfect combustion of the gases, the water-jacket of the cylinder had to be kept at a temperature of from 50° to 60° C., otherwise abnormal explosions were frequent. The speed of the engine was kept constant at about 120 revolutions per minute, and the wire was found to follow the cycle at this speed except at the beginning of the stroke. The number of explosions per minute was from 12 to 14, each explosion being

[*] Phil. Trans. A, 1891.

followed by about 20 blank strokes. The effect of the thorough "washing-out" of the products of combustion from the cylinder and of the hot cylinder jacket was to produce a temperature in the cylinder as high as, if not higher than, if the engine had been working at full load. The small number of working strokes per minute enabled observations to be made with the galvanometer which would not have been possible at much closer intervals of time. The wear and tear on the measuring-wire was reduced, it being a matter of considerable importance to expose the wire to as few explosions as possible.

In all the following experiments the thermometer measuring-wire was placed on the axis of the cylinder and in the centre of the compression space.

Two thermometers were used, both practically of identically the same construction as described above. The results of a number of experiments are given below ; I have selected those which I have reason to believe are the most complete and accurate of the number which I have made. Wherever I have been able, I have given the constants of the thermometers which were determined before and after the experiments ; where it is not given it is because the wire fused before a re-calibration could be made.

January 1st, 1895.

Thermometer No. 5.   Wire 0·003 inch diam.

Air temperature 9° C.   Circulating water, 46° C.

R_0 before, 0·324 ohm. $R_1 - R_0 = 0.1206$. $\delta = 1.52$.
R_0 after,   0·340 ohm.

First Set.			
Percentage of stroke.	Observed Resistance, ohms.	*pt.*	Temperature on air-scale.
10	1·476	948	1120
20	1·443	921	1085
30	1·433	913	1070
40	1·362	854	990
50	1·351	845	975
60	1·299	802	925
70	1·286	791	900
80	1·238	751	850
Second Set.			
10	1·547	1007	1210
20	1·477	949	1120
30	1·466	940	1110
40	1·433	921	1085
50	1·382	871	1010

It will be noticed that the second set show considerably higher temperatures than the first; this is due to the fact that the former set were taken just before darkness came on, and the second after the gas-pressure had risen considerably. Owing to this I have generally worked in the morning, when the gas-pressure is generally steady except when there is a sudden fog.

January 2nd, 1895.

Thermometer No. 4.   Wire 0·0025 inch diam.
Circulating water 50° C.

R_0 before, 0·5216 ohm. R_1 before, 0·7153 ohm. δ before, 1·397.
R_0 after, 0·5357 ohm. R_1 after, 0·7328 ohm. δ after, 2·09.

Percentage of stroke.	Observed Resistance, ohms.	*pt.*	Temp. on air-scale. $\delta = 1·74$.
10	2·474	998	1245
20	2·455	988	1230
30	2·366	942	1150
40	2·306	912	1120
50	2·248	882	1060
60	2·128	820	970
70	2·108	810	950

January 4th, 1895.

Thermometer No. 4.   Wire 0·0025 inch diam.
Air temperature 10° C.   Circulating water 55° C.

$R_0 = 0·530.$ $R_1 - R_0 = 0·1971.$ $\delta = 1·74.$

Percentage of stroke.	Observed Resistance, ohms.	*pt.*	Temperature on air-scale.
Explosion	2·414	956	1189
10	2·483	988	1230
20	2·439	965	1195
30	2·356	923	1130
40	2·338	914	1120
50	2·256	873	1040
60	2·184	836	990
70	2·094	790	920
80	1·960	722	830

Thermometer No. 5. Wire 0·003 inch diam.

$R_0 = 0.332.$ $R_1 - R_0 = 0.1206.$ $\delta = 1.52.$

Percentage of stroke.	Observed Resistance, ohms.	pt.	Temperature on air-scale.
Explosion	1·444	919	1080
10	1·476	949	1120
20	1·451	928	1095
30	1·439	918	1080
40	1·395	818	1025
50	1·392	879	1020
60	1·333	830	955
70	1·268	776	880
80	1·238	751	855

No further experiments were made with this wire as it clearly did not attain the proper temperature.

January 31st, 1895.

Thermometer No. 4. Wire 0·0025 inch diam.
Air temperature 7·5° C. Circulating water 57° C.

R_0 before, 0·562 ohm. $R_1 - R_0$ before, 0·220 ohm. δ before, 1·90.
R_0 after, 0·581 ohm. $R_1 - R_0$ after, 0·227 ohm. δ after, 1·90.

Percentage of stroke.	Observed Resistance, ohms.	pt.	Temperature on air-scale.
10	2·562	893	1100
20	2·595	907	1125
30	2·524	876	1080
40	2·445	840	1020
50	2·360	802	960
60	2·338	792	940
70	2·186	729	850
80	2·151	711	825

February 12th, 1895.

Thermometer No. 5. Wire 0·002 inch diam.
Air temperature 7° C. Circulating water 43° C.

R_0 before, 0·796 ohm. $R_1 - R_0 = 0.283$ ohm.

Percentage of stroke.	Observed Resistance, ohms.	pt.	Temp. on air-scale. $\delta = 1.22$.
10	3·662	1012	1160
20	3·616	996	1140
30	3·477	947	1075
40	3·352	907	1020
50	3·253	868	970
60	3·120	821	910
80	3·071	804	890

This wire was destroyed by accident during my absence before a new value of δ could be determined.

Thermometer No. 4.   Wire 0·0025 inch diam.

$R_0 = 0.592.$ $R_1 - R_0 = 0.223.$ $\delta = 1.90.$

Percentage of stroke.	Observed Resistance, ohms.	*pt.*	Temperature on air-scale.
Explosion	2·529	878	1080
10	2·580	891	1100
20	2·576	890	1100
30	2·499	855	1040
40	2·459	837	1010

The wire partly fused during the observation at 50 per cent. These experiments were made during a period of intense cold, and the indicator diagrams showed the pressures to be lower than usual.   The temperatures were lower than those of Jan. 1–5 or March 7–20, otherwise the fine wire on thermometer No. 5 would not have remained intact so long.

March 7th.

Thermometer No. 4.   Wire 0·0025 inch diam.

Air temperature 10° C.   Circulating water 46° C.

R_0 before, 0·537 ohm. $R_1 - R_0$ before, 0·208.   δ before, 1·81.
R_0 after, 0·551 „ $R_1 - R_0$ after, 0·208.   δ after, 1·75.

Percentage of stroke.	Observed Resistance, ohms.	*pt.*	Temp. on air-scale. $\delta = 1.78.$
10	2·437	913	1115
20	2·450	920	1120
30	2·381	886	1090
40	2·333	861	1060
50	2·304	849	1015
70	2·204	801	940
80	2·113	757	880

March 16th.

Thermometer No. 4.   Wire 0·0025 inch diam.
Air temperature 13° C.   Circulating water 50° C.

R_0 before, 0·551 ohm. $R_1 - R_0 = 0·207$.
R_0 after,   0·551 ohm. δ (determined by sulphur vapour) 1·75.

Percentage of stroke.	Observed Resistance, ohms.	*pt.*	Temperature on air-scale.
10	2·434	909	1100
20	2·354	870	1045
30	2·364	875	1050
40	2·236	833	990
60	2·163	778	910
70	2·057	727	840

I was so doubtful of the second and third points that I repeated the first three with the results below :—

10	2·452	917	1115
20	2·373	879	1055
30	2·369	877	1050

March 20th.

Same thermometer and wire.
Air temperature 13° C.   Circulating water 51° C.

Percentage of stroke.	Observed Resistance, ohms.	*pt.*	Temperature on air-scale.
10	2·481	931	1140
20	2·403	894	1080
30	2·403	894	1080

The temperature was variable throughout this experiment and the wire fused during the observation at 40 per cent.

I consider these experiments to be the most accurate of the whole series.

Towards the end of February I determined to find δ by means of an observation in sulphur vapour ; and as some question had arisen as to the action of the high-temperature gases on the platinum wires, more especially as to the variation of the quantity δ, I gold-soldered a platinum wire 0·002 diameter on No. 5 thermometer, and determined its fixed points and calculated the δ before this wire was placed in the

engine. In every other case the wires had been exposed to the action of the cylinder gases for about half an hour before the determination of the fixed points. In this case the wire had only been exposed to the flame of the blowpipe used in the soldering. The fixed points were $R_0 = 0.7596$; $R_1 = 1.0536$; $\frac{R_1}{R_0} = 1.32$; $R_1 - R_0 = 0.294$; $\delta = 2.93$.

This value of δ seemed so high that I repeated the whole of the points without detecting any error in the previous work. The low value of $\frac{R_1}{R_0}$ together with the high δ seems to indicate that a gold-platinum alloy formed at the junction of the main lead to the fine wire and on the surface of the latter. The thermometer was then placed in the engine on March 16th and gave the following results :—

Percentage of stroke.	Observed Resistance, ohms.	$pt.$	Temperature on the air-scale.
10	3.527	948	1200

After running in the engine some time the fixed points were re-determined with the results given below:—

$$R_0 = 0.786. \quad R_1 = 1.075. \quad R_1 - R_0 = 0.289.$$
$$\frac{R_1}{R_0} = 1.37. \quad \delta = 1.95.$$

From this it will be seen that the action of the gases on the cylinder had been such as to bring the wire into a normal condition, most probably by sweeping off any alloy which had been formed.

I have plotted the results of the experiments, and the curves are given in Plate II. figs. 5, 6, & 7, the corresponding pressure-volume curves being given in figs. 8, 9, & 10. In figs. 5, 6, & 7 the horizontal ordinates show the percentage of the stroke, and the vertical ordinates the temperature in degrees C. on the air-scale, the observed points being marked by small circles. I have divided the experiments up into three groups—the first being from Jan. 1 to Jan. 4, the second from Jan. 31 to March 7, and the last from March 16 to March 20. It will be noticed that those of Jan. 1–4 (fig. 5) show a distinct break in the regularity of the curve, the line falling but little between the 3rd and 4th points on the 0.0025 wire and between the 4th and 5th points on the 0.003 wire, instead of falling regularly throughout as would have been expected. The curves of the second group of experiments (fig. 6) show no trace of irregularity ; while those of the third group (fig. 7)

show a strongly marked variation between the 2nd and 3rd points. Several explanations of this singularity have suggested themselves to me, but I do not consider them to come within the scope of this paper. I hope to make further experiments bearing on this matter, and to obtain more data on the subject. The results of the experiments of Jan. 31 to March 7 are chiefly interesting as showing the close concordance of temperatures registered by wires of such different thermal capacity, especially when it is remembered that the source of heat used was a very variable one, the pressures, as shown on the indicator cards, varying from day to day, and also during the day, owing to the varying gas-pressure and quality.

I would also point out that a difference of 100 degrees shown on the thermometers corresponds to a distance of about $\frac{1}{12}$ inch on the indicator cards.

In conclusion I must express my thanks to Messrs. Johnson and Matthey for the trouble they have taken in drawing down the wires, several of which were of special diameters. I should have been quite unable to carry out costly experiments of this kind had it not been for the liberality of my brother, Mr. H. R. J. Burstall, who has provided me with the necessary funds. The apparatus has been designed and carried out in conjunction with him; and I wish to express my sincere indebtedness to him for his many suggestions, which have made these experiments possible.

XXIV. *On the Constituents of Clèveite Gas.* By Professors C. RUNGE *and* F. PASCHEN, *of Hannover*[*].

SINCE our communication about the Spectrum of Helium[†], we have succeeded in constructing materially better Geissler tubes, which show only traces of impurities, and which emit the light of the gas itself with the greatest brightness. With these new tubes it has not only been possible to explore the infra-red portion of the spectrum as far as $10\,\mu$ with the bolometer, and to discover both of the first members of the two series which, according to our formula, should have wave-lengths of about $1 \cdot 11\,\mu$ and $2 \cdot 03\,\mu$, and which have been found at the positions $1 \cdot 120\,\mu$ and $2 \cdot 040\,\mu$, but, besides, the connexion of the other lines of the spectrum comes out with full distinctness.

The doubts we expressed in our former communication in connexion with the series beginning with 7065 have been confirmed. The two lines there indicated as of questionable origin belong to hydrogen, and the lines 7065 and 5048 belong to two distinct series, which with four others now embrace all the lines of the spectrum.

The following list (see Appendix) contains the newly discovered lines, and those of which the connexions with them have now been ascertained.

The other series of lines can also be traced farther in the new tubes.

We have, accordingly, here to do with six series, among which it twice happens that two series converge towards the same place. Two of these converging series, namely, those beginning at 7065 and at 5876, consist of double lines with equal differences of oscillation-frequencies *. We associate these with the remaining one which has double lines, that which begins at $1 \cdot 12 \mu$ in the infra-red. Two at all events of the three other series have no double lines ; they diverge from the same situation, and we unite them with the remaining series into a second system †.

Both the systems prove to have a similar appearance, and all the lines of the first system are stronger than the corresponding lines of the second system.

Further, it appears that both these spectra are very similar to the spectra of the alkalies. In the spectrum of each of the alkalies we find two " Subordinate Series " (of lines that are double, with the exception of the lithium spectrum in which no pairs have been observed) accompanied by a much stronger " Principal Series." The Subordinate Series diverge from the same situation, and the lines of the brighter of them are more closely spaced. On the other hand, the Principal Series extends farther in the more refrangible direction. All

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* *Note by the Translator.*—The presence of double lines in a series seems to indicate that the single motion in the gas which originates the whole series consists of partials, each of which is in general elliptic ; becoming linear when the constituents of the double lines are of equal intensity, and circular when, as in lithium, one of them vanishes. That the double lines have equal intervals on a map of oscillation-frequencies seems to betoken that the path of that motion in the molecules of the gas to which the series is due is affected by an apsidal shift. See ' Scientific Transactions of the Royal Dublin Society,' vol. iv. (1891) p. 571.

† *Note by the Translator.*—In the diagram the second system is uppermost, next to the hydrogen spectrum ; and the first system, which contains the helium line, is under it, next to the lithium spectrum.

this we find to be the case in both our systems (see the figure). We can distinguish in each of them two Subordinate
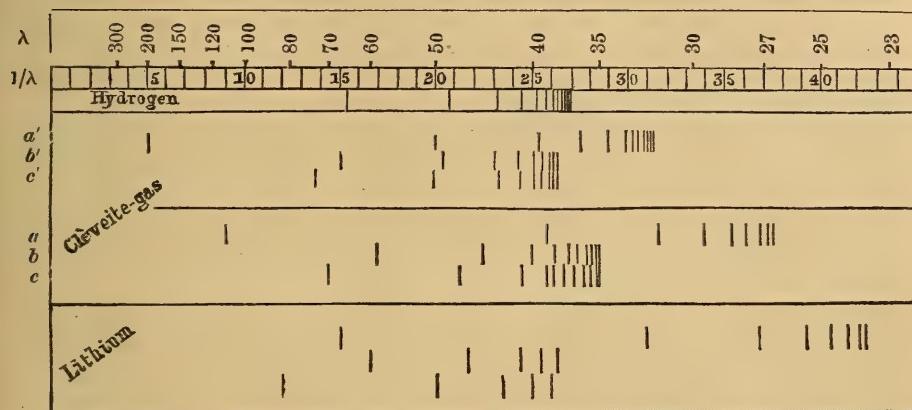
Series diverging from the same situation, of which the brighter is the more closely spaced. Moreover, each system contains a Principal Series whose lines are stronger than those of the Subordinate Series, and which extends to shorter wavelengths.

From the similarity of the two systems to the spectra of the alkalies, we do not mean to infer a chemical relationship. But we seem justified in ascribing the two systems of series to distinct constituents in the gas. Following the astronomers, we should give the name of Helium to that constituent only which emits the yellow line D_3.

If these views are correct, we may venture a further conjecture (based upon the analogy of other spectra) as to the place of the two constituent gases in the series of chemical elements. Since the gas is always present in the sun's chromosphere, it is at all events of low density. This follows also from the determinations of the density of the gas which have been up to the present made, although they have led to discordant results. Clève has found 2·02, Ramsay 3·89 *, referred to the density of hydrogen as the unit. Ramsay regards the gas as monatomic, on account of the velocity of sound in it : and, assuming this, the atomic weight would be 4·04 according to Clève's determination, and 7·78 according

Note by Translator.—More recent determinations by Professor Ramsay, after careful purification of the gas, are given in a paper read before the Chemical Society on the 20th of June, but were not accessible at the time Professors Runge and Paschen wrote their paper. The mean of these determinations gives 2·181 as the density, with a probable error not exceeding 0·05. See 'Nature,' of August 1st, 1895, p. 332.

to Ramsay's. We regard Clève's determination as the more trustworthy, since his Geissler tubes showed no argon lines, and since Ramsay's material, as he states, was not wholly free from nitrogen ; and we shall assume that the atomic weights of both the constituents lie at all events between those of hydrogen and lithium.

So far as it has been possible hitherto to analyse the spectra of elements into series, the series, in the spectra of those chemical elements which follow one another according to atomic weights in a row of the Mendeléeff table, seem on the whole to proceed with increasing atomic weights to shorter wave-lengths. The reverse is the behaviour within a group of related elements as, for example, Li, Na, K, Rb, Cs. We shall in the diagram place the spectra of our two systems between the spectra of hydrogen and lithium in such an order that in going from hydrogen to lithium the series shall proceed to shorter wave-lengths. We should then say that the system next to the series of hydrogen corresponds with the smaller atomic weight rather than the system next lithium.

Helium would, on this view, be the heavier of the two constituents. This is in accordance with an observation we made when filling the Geissler tube. The connecting tube contained a plug of asbestos to keep from the exhausted tube the heavier impurities, which diffused more slowly through the plug. It now appeared, on first opening the cock, that a greenish light was radiated, and in a small direct-vision spectroscope the line 5016 was seen equal in brightness to the yellow line. But, as more gas streamed in, the tube became yellow, and the line 5016 was outshone by 5876. The lighter constituent, whose brightest line in the visible part of the spectrum is 5016, had diffused quicker through the plug. Moreover, Deslandres has already expressed the opinion that the two lines 5016 and 5876 belong to different elements, on account of the varying ratio of their intensities in different parts of his Geissler tubes.

We see a further confirmation of the conclusion that the two systems correspond to different elements in the circumstance that those lines of our spectrum which appear with the most persistence in the chromosphere of the sun, all belong to one system, viz. to the helium system ; whereas those lines of the other system which up to the present have likewise been observed in the chromosphere, occur much less frequently according to Young.

From the series, as presented in the diagram, a conjecture may be formed as to the magnitudes of the atomic weights.

It must be admitted that the inference rests on the supposition that we are right in regarding the hydrogen series as a Principal Series, and this is so far hypothetical, that no Subordinate Series have been found. But if we may assume this, the four Principal Series in the diagram seem to proceed by equal steps towards shorter wave-lengths, from element to element, from hydrogen to lithium. We may perhaps infer similar differences between the atomic weights. This would assign an atomic weight of about 3 to the lighter constituent, and an atomic weight of about 5 to helium ; and, if the two constituents are present in nearly equal quantities in the Clèveite gas, this would agree with the determination by which Clève found the atomic weight to be 4.

We are quite conscious that this conjecture about the atomic weights has not yet a satisfactory foundation. Nevertheless we believe that it merits some consideration. Inferences from the spectrum of an element to its chemical properties will have a surer basis when a mathematical theory can be given of the form of the oscillation upon which the series depend.

Appendix.

In this appendix are brought together all the determinations published by the authors whether in the paper of which the foregoing is a translation, or in the preceding one.

The Series are here placed in order, a, b, and c belonging to helium gas, and a', b', c' to the other constituent of Clèveite gas. a and a' are the Principal Series, b and b' the brighter, and c and c' the less bright of the two Subordinate Series. Two corrections have been made in Series (a) which were furnished by the authors in manuscript.

Series (a).

λ.	$1/\lambda$.	Difference.
1·120 μ.	8928·6	
3888·97	25713·8	16786·5
3888·76	25715·1	
3187·98	31367·8	5654·2
3187·83	31369·3	
2945·35	33951·8	2584·0
2945·22	33953·3	
2829·32	35344·2	1392·9
2829·16	35346·2	
2764·01	36179·3	834·4
2763·91	36180·6	
2723·3	36720	539
2696·5	37085	365
2677·1	37354	269

Series (a').

λ.	$1/\lambda$.	Difference.
2·040 μ.	4902·0	
5015·73	19937·3	15035·3
3965·08	25220·2	5284·4
3964·84	25221·7	
3613·89	27671·0	2450·2
3613·78	27671·9	
3447·73	29004·6	1332·7
3354·7	29809	804
3296·9	30332	523
3258·3	30691	359
3231·3	30947	256
3213·4	31120	173

Series (b).

λ.	1/λ.	Hydrogen. 1/λ.	Differ- ence.
5876·206	17017·78		
5875·883	17018·72	15236·8	1781·9
4471·85	22362·11		
4471·66	22363·06	20569·8	1793·3
4026·52	24835·34		
4026·35	24836·39	23038·0	1798·4
3819·89	26178·76		
3819·75	26179·72	24379·2	1800·5
3705·29	26988·44		
3705·15	26989·46	25187·3	1802·2
3634·52	27513·95		
3634·39	27514·93	25712·6	1802·3
3587·54	27874·25		
3587·42	27875·19	26071·5	1803·7
3554·5	28133	26330	1803
3530·6	28324	26520	1804
3512·6	28469	26666	1803
3498·7	28582	26780	1802
3487·8	28671	26869	1802
3479·2	28742	26940	1802

Series (b').

λ.	1/λ.	Difference.
6678·1	14974·3	
4922·08	20316·6	5342·3
4388·11	22788·8	2472·2
4143·91	24131·8	1343·0

Series (c).

λ.	λ (continued).
7065·77	3599·59
7065·51	3599·45
4713·39	3563·26
4713·17	3563·11
4121·15	3536·9
4120·98	3517·5
3867·77	3502·5
3867·61	3490·8
3733·15	3481·5 ?
3733·01	
3652·29	
3652·15	

Series (c').

λ.
7281·8
5047·82
4437 73
4169·12
4024·14
3936·1
3878·3
3838·2
3808·3 ?

Notes.

1. The rays $1·120\,\mu$ and $2·040\,\mu$ were determined with the bolometer.
2. Of these $1·120\,\mu$, the head of the Principal Series of helium gas, is the strongest line in the spectrum produced by the mixture of the two gases.
3. The first pair of the lines in Series (c) were determined photographically on specially sensitized plates.
4. On the other hand, the position of the first line in Series (c') is from a preliminary determination by an eye-observation made with a small Rowland's flat grating.
5. The hydrogen lines inserted for comparison with Series (b) are determinations by Ames ; see Phil. Mag. of July 1890.

XXV. *The Variation in the Electrical Resistance of Bismuth, when cooled to the Temperature of Solid Air.* By JAMES DEWAR, *M.A., LL.D., F.R.S., Professor of Chemistry in the Royal Institution, &c.,* and J. A. FLEMING, *M.A., D.Sc., F.R.S., Professor of Electrical Engineering in University College, London* *.

[Plate V.]

IN the course of investigations on the Electrical Resistance of pure metals and alloys at low temperatures made during the years 1892 and 1893, the results of which were communicated to the Philosophical Magazine †, extensive examination was made by us of the variation in specific electrical resistance exhibited by most of the ordinary metals when cooled to temperatures approaching the absolute zero. In the course of this research the abnormal behaviour of bismuth with regard to its variation of specific resistance with temperature was noted, and in a further research on the Thermo-electric powers of metals and alloys at low temperatures, the results of which were communicated to the Philosophical Magazine recently ‡, it was noticed that the curves representing the thermo-electric power of bismuth, both for pure and for commercial specimens, presented a discontinuity at temperatures lying between about −70° and −100°. We were therefore recently led to make a more careful examination of the variation of electrical resistance of bismuth when cooled down to the temperature of solid air, some of the results of which are of sufficient interest to communicate, although the investigation is still in progress, and much remains to be done to complete it. A sample of very pure bismuth was kindly prepared for us by Mr. George Matthey, by the reduction of the oxide, an analysis of which showed very small traces of iron as the only impurity. This bismuth, which was the same as that used by us in our thermo-electric experiments, was pressed into wire by a steel press, two sizes of wire being prepared, one having a diameter of about 0·067 centimetre, and the other a diameter of 0·049 centimetre. Lengths of these wires were mounted up in an appropriate form for taking the electrical resistance when measured

* Communicated by the Authors.

† Dewar and Fleming, Phil. Mag. 1892, 5th series, vol. xxxiv. p. 326, " On the Electrical Resistance of Pure Metals, Alloys, and Non-Metals at the Boiling-point of Oxygen ; " also Phil. Mag. 1893, 5th series, vol. xxxvi. p. 271, " The Electrical Resistance of Metals and Alloys at Temperatures approaching Absolute Zero."

‡ Dewar and Fleming, Phil. Mag. July 1895. " Thermo-Electric Powers of Metals and Alloys between the Temperatures of the Boiling-Point of Water and the Boiling-point of Liquid Air."

in liquid or in solid air, or at any other temperature up to +100° C.

Amongst other specimens a wire was pressed from some commercial bismuth, supposed to be fairly pure, which will be distinguished by being called Griffin's Bismuth; the diameter of this last wire was about ·066 centimetre. The diameters of these wires were carefully measured with a microscope-micrometer in about twenty different places, the lengths of the wires used being about 30 or 60 centimetres. The sample of pure bismuth prepared for us by Mr. George Matthey will be distinguished by speaking of it as Matthey's bismuth, the thicker of the two wires being called A and the thinner B. The dimensions and mean diameters of the pressed wires, which were used just as they came from the press, were as follows:—

Sample.	Length. centim.	Mean diameter. centim.
Matthey's Bismuth (Pure), A ...	61·25	0·06713
Matthey's Bismuth (Pure), B ...	32·70	0·04926
Griffin's Bismuth	52·90	0·06625

In addition to these samples of pressed wires, other specimens were prepared by drawing melted bismuth up into fine glass tubes and making a suitable connexion with the bismuth for the purpose of an electrical resistance measurement by means of tinned copper wires melted in to the ends of the bismuth specimen. These samples of bismuth then had their electrical resistance measured with a Wheatstone bridge in the usual way, the temperature of the specimen being taken at the same time by means of a platinum thermometer, consisting of a platinum wire closely in contact with the specimen of bismuth. All the temperatures which are given in the following paragraphs have been converted into platinum temperatures, taken in terms of our standard platinum thermometer P_1, the electrical constants of which were given by us in the paper on the Thermo-electric powers of metals (see Phil. Mag. July 1895). Temperatures so measured are distinguished by the letter P_1 placed after the number denoting the temperature. The electrical resistance of the bismuth specimens, all proper corrections being made for the resistance of the connecting wires, was taken at a large number of temperatures lying between the boiling-point of water (100° C.) down to the temperature of solid air, which, in terms of our standard platinum thermometer P_1 is about $-233° P_1$ to $-235° P_1$. From the known dimensions of the bismuth wires the volume specific resistance of the metal was calculated at these different temperatures, and the reduced observations for the three specimens above mentioned are given in the following tables:—

Commercial Bismuth (Griffin's).

Volume Specific Resistance in C.G.S. units.	Temperature in Platinum degrees.	Volume Specific Resistance in C.G.S. units.	Temperature in Platinum degrees.
190700	+95·0	185050	− 96·9
186850	+84·6	188450	−107·9
180350	+66·6	190050	−111·7
176450	+47·0	193800	−123·5
176200	+46·5	195400	−128·1
175200	+41·2	199700	−140·0
173650	+34·0	200400	−143·9
172000	+21·3	205400	−157·0
172300	+18·8	207000	−162·0
171450	+ 5·2	211450	−180·0
171050	− 2·2	211750	−184·0
171100	− 6·8	212800	−196·6
171650	−25·0	212800	−196·8
172050	−32·7	212050	−213·2
173400	−43·0	212100	−215·5
173700	−47·3	211700	−217·1
176050	−59·6	211500	−220·1
176700	−63·3	210900	−222·5
179050	−75·1	209700	−228·5
180100	−79·1	208900	−232·8
184400	−92·9	208950	−233·2

Pure Bismuth (A) (Matthey's).

Volume Specific Resistance in C.G.S. units.	Temperature in Platinum degrees.	Volume Specific Resistance in C.G.S. units.	Temperature in Platinum degrees.
202550	+ 96·4	183350	−135·0
185100	+ 56·0	186000	−139·0
174200	+ 17·8	188850	−145·9
171100	+ 5·2	193100	−151·6
169750	− 1·8	197450	−156·6
168150	− 9·7	200650	−160·8
166900	− 16·9	204800	−165·8
166550	− 20·5	208250	−170·5
166300	− 24·9	211350	−173·9
165850	− 30·0	213950	−176·8
165600	− 33·0	217100	−179·8
165400	− 37·0	220200	−183·0
165050	− 42·5	222500	−186·3
164800	− 45·0	225300	−188·9
164750	− 47·0	228150	−192·0
104750	− 53·0	229300	−192·7
164900	− 58·4	229850	−193·3
165200	− 65·0	234800	−197·0
165850	− 69·3	242150	−202·6
166150	− 74·5	248150	−207·9
167300	− 81·4	264400	−219·3
168600	− 89·1	266250	−220·8
169400	− 95·0	267900	−222·0
171100	−101·8	276700	−227·1
175150	−114·0	288450	−232·0
176950	−120·1	293100	−234·2
178950	−124·9	294300	−234·85
181150	−130·4	294300	−234·9

Pure Bismuth (B) (Matthey's).

Volume Specific Resistance in C.G.S. units.	Temperature in Platinum degrees.	Volume Specific Resistance in C.G.S. units	Temperature in Platinum degrees.
175100	+49·2	150600	− 87·9
174850	+48·0	151300	−100·5
165100	+18·8	151300	−103·9
163050	+11·3	152000	−114·8
161550	+ 3·6	152850	−118·8
161250	+ 1·3	154950	−132·2
158400	−11·5	155900	−136·1
157900	−18·3	159450	−148·1
153750	−36·5	161200	−152·2
153300	−40·0	166300	−168·0
152350	−51·6	169850	−174·9
152050	−55·3	179550	−193·4
151000	−66·8	181000	−196·2
150850	−71·0	181000	−196·8
150500	−83·3		

The above numerical results are set out in the form of three curves (see Plate V.). It will be seen that the specific electrical resistance of all the bismuth specimens taken from 100° C. downwards gradually diminishes to a point which, in the case of the specimen of pure bismuth " A " was about 50° P_1, and in the case of the specimen " B " about −83° P_1. After these temperatures had been reached, further cooling *increased* instead of diminishing the electrical resistance of the A and B bismuth, until, at the lowest temperature reached by the employment of large quantities of solid air, the electrical resistance of the specimen " A " had become increased by nearly 80 per cent. of its minimum resistance, and at the same time the mean temperature coefficient had become very large, and of course negative. It may be noted that the melting-point of solid air, as determined by our standard platinum thermometer, is −232°·2 P_1, liquefaction taking place under a pressure of 14 millim. of mercury. The boiling-point of liquid air under a pressure of 746 millim. is −209°·75 P_1. The same general facts were observed in the case of the specimen of pure bismuth " B," only in this instance the temperature was not taken below about −200° P_1. As regards the commercial bismuth (Griffin's) the curves show that after reaching a minimum point, which for that specimen appears to occur at about 0° C., there is another point of inflexion in the resistance-curve in the neighbourhood of −200° P_1, after which the resistance again diminishes. In the case of each

of these specimens the resistance measurements were repeated many times, and in both directions, to obtain an assurance that the relation of resistance and temperature was perfectly definite, and that proof might be obtained that all the three specimens of pressed bismuth wire as well as the bismuth melted in the tubes, did not undergo any permanent change in their condition by the action of the low temperature, but that there was a definite relation between temperature and electrical resistance in the manner shown in the curves. Similar experiments made with pure antimony drawn up into glass tubes did not show the appearance of any minimum resistance for any temperature between $0°$ and $-200°$ P_1. In no other case amongst all the metals and alloys examined by us has any phenomenon presented itself similar to that shown by the above specimens of pure bismuth. So far, therefore, as these investigations have gone they show that the behaviour of bismuth at low temperatures in respect of electrical conductivity is anomalous. The temperature-resistance curves of these specimens are quite different to those of other pure metals. In our first communication on the electrical resistance of metals (see Phil. Mag. October, 1892) we showed that carbon taken in the form of a carbon filament from an incandescent lamp increases its resistance continuously when cooled down to the boiling-point of oxygen, and we suggested that for pure non-metals continual lowering of the temperature towards the absolute zero would in all probability continually increase the specific electrical resistance. In the specimens of pure bismuth A and B there is no indication at the lowest temperature reached, viz. $-235°$ P_1, that the resistance lines for this pure bismuth would have another point of inflexion. If, then, the specific resistance of these samples of pure bismuth goes on increasing continuously down to the absolute zero of temperature, as it would appear to do, in that respect they behave like a non-metal, having, however, a very much larger temperature coefficient than carbon. The behaviour of bismuth in a magnetic field in regard to electrical resistance, and also the fact that different specimens of bismuth have in some cases positive and in other cases negative temperature coefficients at temperatures above $0°$ C., has been examined by other observers. Without entering into any historical statement of the course of investigation in this matter, brief reference may be made to two papers on this subject which have a bearing on the facts here described by us. In 1886 an experimental study of the influence of magnetism and temperature on the electrical resistance of bismuth, and also of its alloys with

lead and tin, was described by M. von Aubel (see Phil. Mag.
1888, 5th series, vol. xxv. p. 191). He studied the electrical
resistance of certain specimens of pure bismuth in the form
of rods slowly cooled, and for temperatures between 17°·2 C.
and 70°·8 C. found a negative coefficient for some of these
specimens. In the case of rods of pure bismuth which had
been tempered between temperatures 15°·2 C. and 69°·7 C.
he found a positive temperature coefficient within these limits;
that is to say, in the first case heating the bismuth decreased
its resistance, and in the second case heating the bismuth
increased its resistance between the stated limits of tempera-
ture. In none of the samples of bismuth examined by us
have we found a negative temperature coefficient for tem-
peratures above 0° C.

For a certain specimen of compressed bismuth wire
M. von Aubel found the resistance practically constant be-
tween 16°·8 C. and 76° C.; but on melting, cooling, and
annealing the same specimen it acquired a positive tempera-
ture coefficient between these limits. M. von Aubel examined
the electrical resistance of certain bismuth-lead-tin alloys,
and he came to the conclusion that the cause of these anoma-
lies in the temperature coefficient of bismuth was the varying
physical condition of the bismuth, and not the presence of
impurities. In 1894 Mr. J. B. Henderson published a paper
" On the Effects of Magnetic Fields on the Electric Con-
ductivity of Bismuth " (see Phil. Mag. 1894, 5th series,
p. 488), and he gives a series of curves showing the tempera-
ture variation of bismuth when taken in magnetic fields of
different strengths. For a certain specimen of bismuth wire,
and for a certain magnetic field-strength of about 10,000
C.G.S. units, his curves indicate a point of minimum resist-
ance for the bismuth. Taking the bismuth at a certain tem-
perature, the temperature coefficient at that point in a zero
magnetic field was found to be positive ; but on gradually
increasing the strength of the magnetic field in which the
bismuth was immersed the temperature coefficient finally
became negative. One point of interest, then, in connexion
with these investigations is whether the specific resistance
of bismuth always presents a minimum value, and whether the
temperature at which this minimum value occurs depends
upon the strength of the magnetic field in which the
bismuth is immersed as well as upon the physical condition
of the metal. In the case of the two wires of pure bismuth
" A " and " B ' used by us, the diameters of the wires were
different, and the pressures under which they were formed,
and therefore the physical condition in the interior of the

wire, was no doubt also different. Hence although both these wires present a point of minimum electrical resistance, the temperature at which this occurs is not identically the same. Another point of interest is that the temperature at which a discontinuity was found by us in the thermo-electric line of the pure bismuth, and which was found to be about −80° C., is also approximately the point at which the resistance-temperature coefficient of the same bismuth becomes sensibly negative. It is therefore clear that at this temperature a critical point is reached for this particular sample of bismuth, and below this point the bismuth undergoes a physical change which affects its thermo-electric value as well as its resistance-temperature coefficient. These investigations indicate that the electrical behaviour of bismuth in certain states at and below particular temperatures is irregular, and that further study is necessary to arrive at a complete explanation of the facts. It has been pointed out by one of us (see Friday Evening Discourse at the Royal Institution, by Professor Dewar, "On the Scientific Uses of Liquid Air," Jan. 19, 1894) that the tensile strength of very many metals is greatly increased by cooling them down to the temperature of liquid oxygen, but that there is a very marked decrease in the tensile strength of bismuth as well as of antimony and some other metals when taken down to the same low temperature. It is interesting to note that bismuth, which, at any rate in certain states, presents the anomaly of a discontinuity in its curve of thermo-electromotive force at a certain low temperature, has also at about the same temperature a change of sign of the temperature coefficient, and becomes in addition exceedingly brittle below that temperature.

In an interesting paper on the Mechanism of Electrical Conduction (see Phil. Mag. ser. 5, 1894, vol. xxxviii. p. 57) Dr. C. V. Burton makes reference to our former experiments on the resistance of pure metals, and states and proves a theorem to the effect that at the absolute zero of temperature every substance must have either infinite specific resistance or infinite conductivity. In the samples of bismuth A and B we have before us a material which exhibits, as far as we can judge, a tendency in its specific resistance to continually increase as it is cooled to temperatures lying below about −80°. In this respect it resembles a non-metal, and the question arises whether this is the proper characteristic behaviour of pure bismuth, or whether in any other physical condition it would show the normal quality of pure metals in decreasing its specific resistance regularly as it is cooled towards the absolute zero.

With the object of ascertaining this we have also tested some very pure bismuth kindly sent to us by Mr. Edward Matthey, and which was prepared by the reduction of the oxychloride. This being pressed into wire was found to give a resistance-temperature curve very similar in general form to that marked Griffin's Bismuth in Plate V. The resistance decreased down to about 0° C., and then increased again when cooled to about −160°, and finally decreased again. It is clear, therefore, that the specimens of bismuth, viz. that prepared for us by Mr. George Matthey from the oxide and that prepared by Mr. Edward Matthey from the oxychloride, and which are both very pure, behave quite differently at very low temperatures with regard to their electrical conductivity. We have also examined the variation of a sample of bismuth prepared electrolytically, but the result of this examination we reserve until the observations have been confirmed on other samples of electrolytic bismuth. One fact of considerable interest has presented itself in studying the action of a magnetic field on the electrical resistance of bismuth cooled to low temperatures. It is well known that the electrical resistance of bismuth is increased by being immersed in a magnetic field. Taking a sample of the pure (Matthey) bismuth wire, we measured its electrical resistance at 18° C. in the earth's field and when placed transversely in the field of an electromagnet, and found an increase of resistance due to the field in the ratio of 1·361 to 1·434, or about 5 per cent. The same sample was cooled in liquid oxygen, and measured again in the same fields. The resistances were then in the ratio of 1·478 to 1·858. The increase in resistance in this last case is nearly 25 per cent. Hence the cooling of the bismuth to −182° C. increased the effect of a given magnetic field in altering its resistance about five times.

Another experiment was made to ascertain whether increased pressure on the surface of the bismuth affected its resistance. When a sample of pure bismuth wire was subjected to an external surface-pressure of 300 atmospheres, a very slight but definite increase of resistance was found, which disappeared instantly on removing the pressure.

The above described observations show that there is a very marked difference between different samples of bismuth as regards electrical resistance when subjected to very low temperatures, and that its behaviour at these temperatures in magnetic fields is also abnormal. We propose to reserve further remarks on this subject until we have completed the

experiments in progress on electrolytic bismuth. We expect then to be able to state the results obtained for specimens of bismuth of known chemical purity, and to distinguish between those effects which are due to physical condition and those, if any, arising from the presence of minute traces of impurity.

XXVI. *Notices respecting New Books.*

A Geological Inquiry respecting the Water-bearing Strata of the Country around London, with Reference especially to the Water-supply of the Metropolis; and including some Remarks on Springs. By JOSEPH PRESTWICH, *F.G.S.* 8vo, ix & 238 pages. Gurney and Jackson : London, 1851–1895.

THIS useful work was first published in 1851, and is now re-issued, for reasons given in the Preface, with some additions, by the energetic author Dr. J. Prestwich, F.R.S., &c. &c., who has greatly enlarged his experience in this and other branches of Geology during the long interval of forty years, occupied with active research, including the work of his Professorship in the University of Oxford. The large plate engraved in 1851 was accidentally destroyed before a sufficient number of copies were printed for the book ; and the remainder of the work was put aside, and the plate not reproduced, because one of the sections of the plate (No. 1, from Sussex to Bedfordshire) was proved to be incorrect, the palæozoic rocks having been discovered to be within reach under London. It was thought, too, that this error affected the long section (No. 2 from Wilts to Essex) ; but these old underlying rocks are really so much limited in area that the western portion of the district traversed by the section is properly represented in it ; and the inference as to the possibility of a considerable supply of water being obtainable from the Lower Greensand there still holds good. For this reason the remainder of the printed matter of the book is now issued, without the plate, but with a few new pages (pp. v to ix).

There is now proved to be a belt, variable in width, of water-carrying Lower Greensand encircling the area of underground palæozoic rocks, over which borings do not give so large a water-supply as the Lower Greensand can give. These sand beds extend under the Chalk and Tertiary strata and beyond their outcrop ; thus receiving the necessary rainfall. Their exact yield of water, however, has not been yet ascertained. A certain amount has been obtained by boring in the Lower Greensand, eastward of London, at Shoreham, Strood, Frindsbury, and Loughton. In the western division of the London Basin the recent boring at Wingfield, not far from Ascot, affords ample proof that there exists a large underground supply, as indicated by nearly 3000 gallons in the 24 hours,

with pressure forcing the water seven feet above the surface of the ground.

Dr. Prestwich considers that with a good bore-hole in the Lower Greensand of the Godalming and Hindhead district, a large supply is obtainable, as he originally anticipated. Also that the same strata in the district westward of Leatherhead and Windsor are available for a good water-supply.

Geological Survey of Canada.—*Annual Report, New Series*, Vol. VI. *Reports* A (1892), A (1893), J, Q, R, S. 1892-93. 8vo. Ottawa. 1895.

THE Reports "A," "A" summarize the operations of the Geological Survey for the years 1892 and 1893 respectively. The Report "J," by F. D. Adams, treats of the geology of a part of Central Ontario, especially noticing the metallic ores of the district. The geological structure of South-western Nova Scotia is the subject of the Report "Q," by L. W. Bailey, with a map. Chemical examinations of Canadian rocks and minerals are detailed by G. Ch. Hoffman in Report "R," resulting in useful determinations and assays of numerous rocks, ores, and minerals, including coal, lignite, lava, granite, limestone; ores of iron, nickel, cobalt, gold, and silver; also natural waters, clays, and miscellaneous substances.

In Report "S" E. D. Ingall and H. P. H. Brumell give the statistics of mines and mineral produce, in the Dominion, for 1892, under twenty-seven headings, including mineral waters, petroleum, and natural gas, with eleven plates of appropriate statistical diagrams and plans, illustrative of annual produce and value, especially of gold and silver.

Of the most valuable of the Canadian metallic products, for 1892, are, of metals—Nickel valued at $1,399,956 ; Gold, $907,601 ; and Copper, $826,849; of other materials—Coal $7,184,510 ; Petroleum $982,489 ; Bricks $1,251,934. The total value of the mineral production in 1892 was $18,000,000. In general these products were of less value than they had been in 1891.

The exports of minerals and mineral products in 1892 were valued at $5,229,950. Of the destinations of these materials the chief (in order) were the United States, Great Britain, and Newfoundland. Tables of imported minerals and mineral products are also supplied.

A good Index is appended, which refers to all the Reports.

These reports evidently are, in the first place, the result of careful and conscientious work in the field and the office; and, secondly, they are of considerable value both to the inhabitants of Canada and to scientific and commercial people, who may have at heart the interest of geology and mineralogy, or that of the great Colony itself, or both.

XXVII. *Proceedings of Learned Societies.*

GEOLOGICAL SOCIETY.

[Continued from p. 231.]

April 3rd, 1895.—Dr. Henry Woodward, F.R.S., President,
in the Chair.

THE following communications were read :—
1. 'Physical Features and Geology of Mauritius.' By Major
H. de Haga Haig, R.E., F.G.S.

The greater part of the surface of Mauritius is composed of a
volcanic breccia ; here and there lava-streams occur in the sections
exposed in ravines, and sometimes on the surface. The commonest
lavas are dolerites.

In at least two places, sedimentary rocks occur at considerable
elevations ; in the Black River Mountains at a height of about
1200 feet a clay-slate is found, and near Midlands in the Grand
Port group of mountains a chloritic schist is found at an elevation
of about 1700 feet, forming the hill of La Selle ; the schist is much
contorted, but seems to have a general dip to the south or south-
east.

Evidence of recent elevation of the island is furnished by masses
of coral-reef and beach coral-rock standing at heights of 40 feet
above sea-level in the south, 12 feet in the north, and 7 feet on the
islands situated on the bank extending to the north-east.

The author gives full details of the physical geography of the
island, including the nature and composition of the mountain-
ranges, the depth of the ravines, the occurrence of caverns in the
lavas, and the character of the coral-reef surrounding the island.
Information is furnished concerning the neighbouring islands, and
reference made to the possible former existence of an extensive
tract of land at no great distance from Mauritius.

2. 'On a Comparison of the Permian Freshwater Lamelli-
branchiata from Russia with those from the Karoo Formation
of Africa.' By Dr. Wladimir Amalitsky, Professor of Geology in
Warsaw University.

3. 'Ice-plough Furrows of a Glacial Period.' By W. S. Gresley,
Esq., F.G.S.

The furrows described in the paper occur in Coal-Measures
of North-west Leicestershire. The author considers that they were
formed about the time of the Glacial Period by floating ice.

April 24th.—Dr. Henry Woodward, F.R.S., President,
in the Chair.

The following communications were read :—

1. 'On the Shingle Beds of Eastern East Anglia.' By Sir Henry
H. Howorth, K.C.I.E., M.P., F.R.S., F.G.S.

The author has carefully examined the country around Southwold,
where the beds known as Westleton Beds (which might well have
been associated with the name of Southwold) are developed. He
alludes briefly to the recent shingle, whose pebbles are derived from
the ancient shingles of the cliffs ; the formation of this shingle, he
maintains, may belong to a time not far removed from our own day.
Turning to the Westleton Beds, he notices that they are essentially
' drifts,' the component pebbles not having been shaped on the spot,
but brought as pebbles from elsewhere ; and he gives reasons for
supposing that they were derived from pebbly beds in the Lower
London Tertiary group and in the Red Crag. He also maintains
that the shells of the Westleton Beds and Bure Valley Beds are
derived from Crag deposits. Reasons are given in the paper for
supposing that the pebbles of the Westleton shingle of East Anglia
came from the west, and that this moved eastward from the plateau
of Suffolk towards the sea. It is considered that these beds can
only be explained by a tumultuous diluvial movement.

2. 'Supplementary Notes on the Systematic Position of the Tri-
lobites.' By H. M. Bernard, Esq., M.A., F.L.S., F.Z.S.

3. 'An Experiment to illustrate the Mode of Flow of a Viscous
Fluid.' By Prof. W. J. Sollas, D.Sc., LL.D., F.R.S., F.G.S.

The author, recognizing that it is by a knowledge of the laws of
viscous flow that we must seek to extend our information concern-
ing the movements of flowing ice, conducted an experiment, the
details of which are described in the paper, with a model of a glacier
composed of the modification of pitch usually known as ' cobbler's
wax.' In the model the pitch moved under its own weight over
the horizontal floor of a trough, which was crossed by a barrier
to represent an opposing mountain or the rising end of a lake. The
results of the experiment showed that the movement of the pitch-
glacier was not confined to that portion of it which rose above the
barrier, but extended throughout its mass, and that an upward as
well as forward movement took place as the barrier was approached.
Thus the transport of stones by glaciers from lower to higher levels
was by no means an incredible phenomenon, but a necessary con-
comitant of such simple conditions as those assumed in the ex-
periment.

May 8th.—Dr. Henry Woodward, F.R.S., President,
in the Chair.

The following communications were read :—

1. 'The Stirling Dolerite.' By Horace W. Monckton, Esq.,
F.L.S., F.G.S.

The rock described in the paper forms a mass about 8 miles in
length, with an average width of about a mile ; it is intruded into
the lower part of the Carboniferous Limestone series. There is
little doubt that the Abbey Craig rock, N. of the Forth, is connected
with the Stirling rock ; and there is reason to think that the
igneous rocks of Cowden Hill and of the hills around Kilsyth are
outlying portions of the Stirling rock, being connected with it
underground.

All these patches, as well as the main mass, are for the most part
composed of a more or less coarse-grained dolerite, the marginal
part always becoming finer-grained, whilst the actual edge has
apparently been a tachylyte now devitrified.

The author gives the results of his macroscopic and microscopic
examination of the rocks from various parts of the mass. He
describes rocks from the centre, and also towards the bottom and
top of the main mass, including actual contact-specimens from
the bottom at Sauchie Craig and from the top at Sauchieburn
as well as contact-specimens from minor sheets ; and he infers
that the sequence is somewhat as follows (beginning from the
centre) :—

(i) Coarse-grained ophitic dolerite, forming the greater part of
the mass.

(ii) Fine-grained ophitic dolerite, say 10 to 20 feet from the
margin.

(iii) Basalt with *very little* augite, and with rods of iron-oxide.

(iv) Basalt with porphyritic plagioclase-crystals in a groundmass
of microliths of plagioclase and hairs and rods of iron
oxide, having *no* augite. This occurs as near as $\frac{1}{2}$ inch to
the junction, and as far as 5 inches away from it.

(v) Basalt with porphyritic plagioclase in a grey groundmass,
say $\frac{1}{10}$ to 1 inch from the margin.

(vi) Basalt with porphyritic plagioclase in a groundmass which
is sometimes spherulitic ; about $\frac{1}{10}$ inch thick on the
average.

2. 'Notes on some Railway Cuttings near Keswick.' By J.
Postlethwaite, Esq., F.G.S.

Several cuttings have recently been made on the Cockermouth,
Keswick, and Penrith Railway, chiefly through drift, though some

occur in the Skiddaw Slates, and in one case a diabase dyke (much decomposed) was met with. It is similar in character to a rock exposed about $\frac{1}{4}$ mile west of Troutbeck.

The author describes the drifts as blue clay beneath, and brown clay above, and considers that these two clays were produced during two separate periods of glaciation, with no long interval between. In some places near Keswick water-borne gravel may be seen surmounted by blue clay; this gravel is considered by the author to be of fluviatile origin. A section at Keswick Station is described; it is 130 yards in length, with a slight break in it, 50 yards of the western end being cut back 9 feet to the north. At the point where the break occurs, and for 17 yards eastward, some beds of current-borne materials take the place of the lower part of the blue clay. There is a bed of a very fine brown sediment 1 foot thick; above it is 2 feet of fine sand, and above that a bed of coarse gravel and pebbles, which is succeeded by blue clay of the usual type. The whole of these beds dip south-west, at an angle of about 9°.

The author has searched both blue and brown clays diligently for shells, but hitherto without success.

3. 'The Shelly Clays and Gravels of Aberdeenshire considered in Relation to the question of Submergence.' By Dugald Bell, Esq., F.G.S.

The drifts of this region have been described by Mr. Jamieson, and also in the publications of the Geological Survey. The two authorities agree that the Lower (grey) Boulder Clay of the district was produced by a local glaciation. The Geological Surveyors, however, maintain that the intervening sands and gravels with marine shells were produced during a submergence of 500 feet or upwards, whilst the Upper (red) Boulder Clay was formed by an ice-sheet from the south. Mr. Jamieson, on the other hand, assigns a purely glacial origin to the Middle Sands and Gravels, and considers that the Red Clay (which contains a few fragments of marine shells) indicates a submergence.

The author discusses these views, and maintains that submergence is not proved in the case of either Middle Gravels or Red Clay, but that the former are, as Mr. Jamieson maintained, truly glacial, whilst he advocates the existence of extra-morainic lakes to explain the latter.

May 22nd.—Dr. Henry Woodward, F.R.S., President,
in the Chair.

The following communications were read :—

1. 'On a Human Skull and Limb-bones found in the Palæolithic Terrace-Gravels at Galley Hill, Kent.' By E. T. Newton, Esq., F.R.S., F.G.S.

2. 'Geological Notes of a Journey round the Coast of Norway and into Northern Russia.' By G. S. Boulger, Esq., F.L.S., F.G.S.

The author accompanied the Jackson-Harmsworth Polar Expedition as far as Archangel, and returned by way of the River Dvina. His observations relate mainly to four points:—the origin of the foliation of the Norwegian gneiss; the question of raised beaches on the North-western coast of Norway; the boulders and boulder-formation of Northern Russia; and the Trias of the Dvina valley.

Between Christiansund and Tromsö the author was struck with the wide-sweeping folds of the foliation-planes of the gneissose rocks, which appeared to him more readily explicable on a theory of dynamo-metamorphism of rocks originally in part igneous, than by any process of diagenesis. He notes that the terraces observed in the transverse fjords would be perfectly explained by the formation of ice-dammed lakes, though the terraces of the Gulf of Onega seemed less dubious raised beaches than those of the North-west of Norway. He confirms the views of previous writers that many of the boulders of the boulder-formation of Northern Russia are of Scandinavian origin. The beds on the Dvina consist of sands and loams, often coloured red, with bands of alabaster and anhydrite. The strata are horizontal or inclined at a low angle. North of Ustyug Veliki the strata are marked as Permian on the Russian maps, and those to the south as Trias, but the author saw no perceptible break in the succession.

3. 'On some Foraminifera of Rhætic Age, from Wedmore in Somerset.' By Frederick Chapman, Esq., F.R.M.S.

June 5th.—W. H. Hudleston, Esq., M.A., F.R.S., F.L.S.,
Vice-President, in the Chair.

The following communications were read:—

1. 'On a well-marked Horizon of Radiolarian Rocks in the Lower Culm Measures of Devon, Cornwall, and West Somerset.' By George Jennings Hinde, Ph.D., F.G.S., and Howard Fox, Esq., F.G.S.

In the Lower Culm Measures the basal *Posidonomya*-beds and the Waddon Barton beds with *Goniatites spiralis* consist of fine shales with thin limestones, and above these are the beds which form the subject of the present paper. The Upper Culm Measures consist of conglomerates, grits, sandstones, and shales, with occasional beds of culm. There is evidence of the partial denudation of the Radiolarian rocks during the accumulation of the Upper Culm beds, as indicated by the presence of pebbles of the former in the latter.

The Radiolarian Beds consist of a series of organic siliceous rocks—some of a very hard cherty character, others platy, and yet others of soft incoherent shales. They are spoken of as the Codden Hill beds—a name applied to them by previous writers, though the

authors do not include in this series all the beds which have been referred to it by others. The term 'Grits,' which has been used in connexion with these beds, is a misnomer; there are beds which are superficially like fine grits, but they are found to be radiolarian deposits.

The Codden Hill Beds occur along a comparatively narrow belt of country, a short distance within the northern and southern boundaries between the Carboniferous and Devonian systems. Starting with the northern exposures, the authors give a description of the beds as developed in various localities from the neighbourhood of Barnstaple (Codden Hill itself, situated 3 miles S.E. of Barnstaple, being a convenient starting-point), past Dulverton, to Ashbrittle in West Somerset. On the south the beds are traceable from Boscastle to the neighbourhood of Tavistock, and on the east side of the Dartmoor granite they are found near Chudleigh and Bovey Tracey.

At present there are not sufficient data for estimating the thickness of the radiolarian deposits; but they are probably some hundreds of feet thick, though the whole does not consist of beds of organic origin. In a quarry in the Launceston district 50 feet of radiolarian cherty rock are seen without admixture of shale.

A detailed description of the lithological characters of the rocks of the series is given, and analyses by Mr. J. Hort Player; a marked feature of their composition is the very general absence of carbonate of lime. The microscopic characters of the rocks are also described, and the small amount of detrital matter in the beds of the series is noted.

Forms belonging to 23 genera of radiolaria have been recognized, included in the orders *Beloidea, Sphæroidea, Prunoidea, Discoidea*, and *Cyrtoidea*; in addition a scanty but significant fauna of corals, trilobites, brachiopods, and cephalopods is present in some thin shaly beds near Barnstaple. Nearly all the forms are diminutive. The trilobites are described by Dr. H. Woodward, the brachiopods by Mr. F. A. Bather, and the cephalopods by Mr. G. C. Crick. Of the 25 species of fossils other than radiolaria which have been determined, several are only known elsewhere from the Lower Culm of Germany, while others are common to the Carboniferous Limestone of the British Isles and Belgium.

These fossils tend to confirm the view that the Lower Culm Measures are the deep-water equivalents of the Carboniferous Limestone in other parts of the British Isles, and not shallow-water representatives of deeper beds occurring to the north, as was formerly supposed. In connexion with this it is worthy of note that the deep-sea character of the Lower Culm of Germany, which corresponds with our Lower Culm Measures, was maintained by Dr. Holzapfel even before the discovery of radiolaria in the beds of Kieselschiefer furnished such strong evidence in support of this view.

2. 'The Geology of Mount Ruwenzori and some Adjoining Regions of Equatorial Africa.' By G. F. Scott-Elliot, Esq., M.A., B.Sc., F.L.S., and J. W. Gregory, D.Sc., F.G.S.

Ruwenzori is a mountain between the Albert and Albert Edward Nyanzas. Topographically it is a narrow ridge which extends for about 50 miles in a direction from N.N.E. to S.S.W. Its summit attains a height of 16,500 feet. The western slope is at an angle of 22°; the eastern slope at about one of 4°. The authors describe sections across the ridge at right angles to its trend. These show that Ruwenzori is not volcanic, nor is it a simple *massif* of diorite. Epidiorite occurs only as banded sheets in the schists on the flanks of the mountain, and is not the central rock of the ridge. The strike of the flanking schists seems to run concentrically round the ridge as though the central rock were intrusive into them. The highest rock collected, a coarse-grained granite or granitoid gneiss, may be an intrusive igneous rock, but it may be part of the old Archæan series faulted up; there is nothing in its microscopical characters to separate it from the Archæan rocks, and the authors think it probable that this rock was raised into its present position by faulting. In this case Ruwenzori is simply composed of an orographic block or 'scholl,' which was at one time probably part of a wide plateau of Archæan rocks.

There is abundant evidence of volcanic action around Ruwenzori, for the plains, especially to the east and south-east, are studded with small volcanic cones, arranged on lines which radiate from Ruwenzori.

It is affirmed that evidence points to the former occupation of the Nyamwamba, Mubuku, and Batagu valleys by glaciers, *roches moutonnées* of typical character having been noted in the two former valleys.

The country round Ruwenzori consists of rocks which may be conveniently grouped into two series—one composed of gneisses and schists, and the other of non-foliated sediments. The former (the Archæan series) are of the type that has an enormous extension in Equatorial Africa, and forms the main plateau on which all the sediments and volcanic rocks have been deposited.

The sedimentary rocks are probably Palæozoic, possibly pre-Carboniferous, but in the absence of fossils it would be unsafe to go beyond this statement.

3. 'On Overthrusts of Tertiary Date in Dorset.' By A. Strahan, Esq., M.A., F.G.S.

The results given in this paper were obtained during a re-survey of South Dorset on the 6-inch scale. The disturbances can be divided into two groups,—the one being mainly of Miocene date, and

the other of intra-Cretaceous (between Wealden and Gault) age. The former includes the Isle of Purbeck fold (which is the continuation of the Isle of Wight disturbance), the Ringstead fold, the Chaldon and Ridgeway disturbances, and the Litton Cheney fault. In the latter are placed the anticline of Osmington Mill, the syncline of Upton, and a part of the anticline of Chaldon; farther west the Broadway anticline and Upway syncline, a fault at Abbotsbury, and many other folds come into the same group. These earlier movements led to the well-known unconformity at the base of the Upper Cretaceous rocks.

The Isle of Purbeck fold is accompanied by a large thrust-fault, by which the uppermost zones of the Chalk have been pushed in a vertical position under gently inclined lower zones. On the same line of disturbance at Lulworth Cove, the squeezing-out of plastic strata from a part of the fold where compression has been great, and the folding and packing away of such strata in a part where there was a tendency to gape, is described. Farther west the same disturbance is accompanied by inversion of a great thickness of beds, great compression, with vertical crush-planes and nearly horizontal slide-planes. The latter slope southwards, and the roof has moved northwards and upwards over the floor; these slide-planes have accompanied the phenomena of inversion.

The Ridgeway fold and fault resemble those of the Isle of Purbeck, but for some distance the thrust-plane has split, a part of it cutting into the Oolitic floor on which the Upper Cretaceous rocks were laid down, and causing a wedge of Oxford Clay, Cornbrash, and Forest Marble to be thrust over Wealden, Purbeck, Portlandian, and Kimmeridge Clay.

The Litton Cheney fault is connected with an anticline in the Chalk and Greensand which has been superimposed upon a syncline in Kimmeridge Clay and Corallian.

The intra-Cretaceous disturbances have been distinguished by the fact that Upper Cretaceous rocks rest undisturbed upon them, the difference in inclination amounting sometimes to 40°. This movement may have commenced before the Lower Greensand was laid down, but took place principally between the deposition of that formation and the Gault.

The features produced by the earlier movements were planed down before the Gault was deposited, and have had no share in producing the existing physical geography. The later movements, on the other hand, have determined the lines of drainage and the great physical features of the region.

XXVIII. *The Gladstone " Law " in Physical Optics, and the True Volume of Liquid Matter.* By WALTER HIBBERT, F.I.C.*

ONE of the curious results established in Chemical Optics is that two independent formulæ (those of Gladstone and Lorentz respectively) can be used in the discussion of experimental data relating to the refractive index and the density of a given substance. Neither of them can claim any special advantage. They both have a wide range of application, yet neither holds universally good. Still more curiously, they break down under quite different conditions of experiment.

The Lorentz formula,

$$\frac{\mu^2-1}{\mu^2+2} \cdot \frac{1}{d} = \text{constant},$$

which is able to cover the large variation in density separating a liquid and its vapour, gives erroneous results in the simple case of a liquid whose density is changed by pressure. On the other hand, the Gladstone formula,

$$\frac{\mu-1}{d} = \text{constant},$$

is unique in its power to deal with liquids under varying pressure, but fails in the jump from liquid to vapour.

* Communicated by the Physical Society.

Hitherto no light has been thrown on these anomalies, but this present paper attempts to explain the exceptions in the case of the Gladstone expression, and, incidentally, introduces a physical magnitude which is conveniently described as the " actual volume occupied by one gramme of the substance."

The suggestion of the present argument arose out of a number of experiments carried out by Dr. Gladstone and myself during the last two years. We have examined a great variety of salt-solutions, whose strength varied from saturation down to about 5 per cent.—a dilution limit imposed by experimental error when the hollow-prism method is adopted for obtaining the refractive index.

Our main conclusion, to the effect that the value of $\dfrac{\mu-1}{d}$

for the salt is practically constant, has received special confirmation by the publication of a paper by Kohlrausch and Hallwachs [*], in which they extend the work on about 10 salts to extremely dilute solutions. They used an interference method for determining μ, and a special apparatus for getting d with the necessary accuracy, so that the experimental error is not larger than usual, even when the amount of salt present is not greater than 0·05 per cent. of the solution.

An examination of this body of evidence proved to me that the constancy of $\mu-1/d$ was much greater for an ordinary dissolved salt than for a simple liquid whose density is changed by heat. For example:—

When heptane is heated from 12° to 88° its density changes by about 10 per cent., and the value of $\mu-1/d$ by 0·55 per cent.

Sodium chloride, diluted from 13 per cent. down to 0·03 per cent. (a concentration change of 400 to 1), has its value for $\mu-1/d$ changed by 0·22 per cent. only.

In speculating on this far greater constancy in the case of a dissolved salt, it seemed not unreasonable to regard the solution in the light of Van't Hoff's theory, attributing a pseudo-gaseous condition to the dissolved salt. This at once suggested other comparisons, and led to the following summary statement of all experimental results on the subject :—

1. The Gladstone expression is true in the case of gases whose density is changed by varying pressure [†].

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[*] Wied. *Ann.* 1894, liii. p. 1.

[†] Biot and Arago, *Mem. d. l'Inst.* vii. p. 301 (1806), and Chappuis and Riviere, *Compt. Rend.* ciii. Biot and Arago express their results $(\mu^2-1)v=$ const. But μ^2 is only slightly greater than unity, and therefore $(\mu-1)v$ must also be constant.

2. It is true in the case of liquids whose density is changed by varying pressure *.

3. It is true (or a *very* close approximation) in the case of dissolved salts, especially in dilute solution.

4. It is a less close approximation in the case of simple liquids undergoing thermal expansion.

5. It altogether fails when a liquid is changed into vapour.

On studying the results included in 4, it appeared that they had one point in common. If the variation be expressed in symbols, it may be put in the form

$$e_t = e_0 (1 \pm at),$$

where e_0 and e_t are the values of $\dfrac{\mu - 1}{d}$ at $0°$ and $t°$ respectively.

Examination showed that all good experiments gave a negative sign for the coefficient a. In other words, the value of e always diminishes as the density diminishes. If we put $(\mu - 1)/d = (\mu - 1)v$, where v is the volume of unit mass, we may say that $(\mu - 1)v$ always diminishes as v increases. This statement is still more emphatically true when the liquid becomes a vapour.

Therefore, in classes 4 and 5, whenever v increases the product $(\mu - 1)v$ diminishes. In liquids, where the change in v is not very great, the diminution of the product is small ; but in passing to vapour, where the change in v is enormous, the product $(\mu - 1)v$ undergoes a large diminution. To put the same thing in the inverse sense, the results show that when v becomes comparatively small, there is a marked increase in the product. So stated, they afford criteria by which we may possibly find the cause of the deficiency. The conditions are almost a reproduction of those which led to the second approximation in the case of Boyle's law. Experiment showed that the product pv was only constant when v was comparatively large. As v diminished, there was a tendency for the product to increase, and it became necessary to suppose that the expression pv referred not to the whole space symbolized by v, but to v minus the space occupied by the particles. Hence $p(v - b)$, where b is the actual volume of the matter, has taken the place of pv.

It appeared to me, that the similar experimental results would warrant the introduction of a similar symbol in the Gladstone expression, thus transforming it into

$$(\mu - 1)(v - \beta) = \text{constant.}$$

* Quincke, Phil. Mag. 1884, xvii. p. 65.

Z 2

It is at once apparent that the introduction of β tends to remove the anomalies, and also evident why cases 1, 2, and 3 in the above summary are satisfied by the uncorrected formulæ.

In 1 and 3, that is in the case of gases and dissolved salts respectively, the value β is negligible compared with v.

In 2, owing to the very slight compressibility of the liquids, the changes in v are always exceedingly small. Hence $v - \beta$ will change almost as much as v, if, as is probable, β is not a large fraction of v.

In 4, the case of liquids undergoing thermal expansion, the changes in v are great enough, as compared with the value of β, to cause an appreciable difference between the ratios v/v_1 and $(v - \beta)/(v_1 - \beta)$.

In 5, the case of vaporization, we have v for the liquid comparatively small, changing into a very large value in the vapour. Here there is a decided and altogether disturbing difference between the ratios v/v_1 and $(v - \beta)/(v_1 - \beta)$*.

Evidently, then, if the numerical data are found to be of the right order, the introduction of β will remove the reservations with which the Gladstone law is usually stated. Moreover, the physical conditions under which β needs to be introduced render it probable that β has, or may have, a physical meaning, and is not merely of the nature of an arbitrary constant. But the real justification for introducing β must be, *à posteriori*, by showing that the calculated values are not improbable, and that they have relations to other physical quantities.

We can determine β for any one substance from observations on a liquid at two different temperatures.

Let μ_1, μ_2 be the refractive indices; v_1, v_2 the volumes of unit mass $\left(= \dfrac{1}{d} \right)$ at the temperatures of two experiments,

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* This paper was written out before I recalled the fact that Ketteler suggested the same solution for the discrepancies experienced in applying the expression $(\mu^2 - 1)v = $ constant. Writing it $(\mu^2 - 1)(v - \beta)$ he examined a series of experiments made by Weegmann (*Zeit. phys. Chem.* ii. p. 905). The result was not very encouraging. But I am of opinion that there are two reasons for that discouragement. First, Weegmann happened to work on substances of exceptional density, a fact which ought to foreshadow the probability of exceptional results in any volume deduced from them. Secondly, the expression $(\mu^2 - 1)v$ is surely not so good a basis for the investigation as the simpler one due to Gladstone and Dale. In ordinary liquids it is not so constant; it is not supported by Quincke's experiments on liquids under pressure (*comp.* Sutherland, Phil. Mag. 1888); nor does it render such service in Physical Chemistry as either the Gladstone or Lorentz expression.

and let β have the meaning suggested, then

$$(\mu_1 - 1)(v_1 - \beta) = (\mu_2 - 1)(v_2 - \beta),$$

and

$$\beta = \frac{(\mu_1 - 1)v_1 - (\mu_2 - 1)v_2}{\mu_1 - \mu_2}.$$

This equation shows that the measure of β will depend on differences which we know to be small, and it is at once evident that the best experiments only will be serviceable. Thus, a table of results for carbon disulphide gives the following figures for the temperatures of $0°$ and $40°$ Centigrade ; the data are Ketteler's :—

$$\mu_1 = 1 \cdot 64375, \ \mu_2 = 1 \cdot 61187 \ ; \ v_1 = \cdot 77314, \ v_2 = \cdot 81103.$$

Therefore

$$\beta = \frac{0 \cdot 497709 - 0 \cdot 496245}{0 \cdot 03188} = \frac{0 \cdot 001464}{0 \cdot 03188} = 0 \cdot 0459.$$

Here the difference between the two terms of the numerator is only $\frac{1}{350}$ of either, and as each term involves only the fractional part of the index, any error in μ is multiplied about 900 times in its effect on β.

This makes it imperative to attach weight only to those experiments where special appliances have been adopted to keep the temperature constant during the observations. For this reason I simply allude to the few results I have myself obtained in a few preliminary experiments, reserving data for a fuller discussion. The results here presented depend almost entirely on the work of three sets of observers, namely, Nasini and Bernheimer, Perkin, and Ketteler. It would be invidious for me to single out one of these as more accurate than the others ; their papers show that all the experiments are of a high order of accuracy. It is doubtful, however, whether Perkin's data are not the most serviceable for our present purpose, if only for the reason that the interval of temperature he employed is greater, with the consequence that the differences on which β depends become more marked, and thereby afford greater accuracy.

Table I. is drawn up from a paper by Nasini and Bernheimer*. They were the first to use a jacketed prism, so that their results are the earliest of those suitable for deducing β. One substance in their list—bromonaphthalene—has been omitted, as it stands alone in giving an increase in $(\mu - 1)v$ on heating. It is probable that the limit of experimental error is reached with that substance.

Column 2 gives the temperatures, 3 the densities, and

* *Gaz. Chim. Ital.* xv., 1885.

4 the indices for the line α. Col. 5 gives three values of β as calculated from the two indices for each of the lines α, D, and β. The indices for D and β will be found in the original paper.

TABLE I.

Substance.	Temp.	Density.	μ_α.	$\beta = \dfrac{(\mu-1)v-(\mu_1-1)v_1}{\mu-\mu_1}$.	v at lower temp.	$\dfrac{\beta}{v}$.
Thymol, $C_{10}H_{14}O$.	24°	0·96895	α1·51453	0·0563		
	77·3	0·92838	α1·49189	0·0600		
				0·0623		
				Mean 0·0600	1·0320	0·058
Cinnamic Alcohol, $C_9H_{10}O$.	24·8	1·04017	1·57311	0·077		
	77·3	1·00027	1·54939	0·086		
				0·011		
				0·080	0·96055	0·083
Anethol, $C_{10}H_{12}O$.	14·9	0·99132	1·55559	0·066		
	77	0·94041	1·52526	0 063		
				0·069		
				0·066	1·0087	0·0655
α-Methyl α-Naphthol, $C_{11}H_{10}O$.	14	1·09636	1·61474	0·0566		
	77	1·04661	1·58508	0·0570		
				0·0850		
				0·0620	0·9121	0·0680
Dimethylnaphthalene, $C_{12}H_{12}$.	16·4	1·01803	1·60765	0 0869		
	77	0·97411	1·57901	0·0899		
				0·0893		
				0·0890	0·9823	0·09

The third value (that given by Hβ) for cinnamic alcohol appears to be wrong, and the third value for methyl α-naphthol also, though to a less degree. In calculating the means, I have ignored the first and allowed only half weight to the second of these.

The next table contains all the observations made by Perkin*, whose apparatus was still more perfect than that of Nasini and Bernheimer. The index is quoted here for the line D only, but the quantity β has been calculated from the lines A, C, D, and F. Where a fifth value is given, it is calculated from the line G.

* Chem. Soc. Journ. 1892, pp. 287 & 800.

TABLE II.

Substance.	Temp.	Density.	μ_D.	$\beta = \dfrac{(\mu-1)v - (\mu_1-1)v_1}{\mu - \mu_1}$.	v at lower temp.	$\dfrac{\beta}{v}$.
Heptane, C_7H_{16}	12·2 88·8	0·69026 0·62301	1·39220 1·35197	0·0808 0·0810 0·0813 0·0814 Mean 0·0810	 1·4487	 0·056
Octyl Iodide, $C_8H_{17}I$.	14 88	1·34096 1·25332	1·4922 1·4579	0·0467 0·0476 0·048 0·0475	 0·7457	 0·063
Methylene Iodide, CH_2I_2.	8 87	3·3480 3·1390	1·74935 1·69500	0·0425 0·0429 0·0442 0·0445 0·0440	 0·29868	 0·15
Toluene, C_7H_8	10·7 90	0·87532 0·79949	1·5028 1·45673	0·0677 0·0683 0·0688 0·0709 0·0688	 1·1424	 0·06
Phenyl Chloride, C_6H_5Cl.	9·6 89·2	1·1167 1·0302	1·53103 1·48731	0·0421 0·0533 0·0572 0·0543 0·0577 0·0540	 0·8955	 0·06
Phenyl Bromide, C_6H_5Br.	4·2 89·2	1·5100 1·39638	1·56845 1·52235	0·0458 0·0440 0·0464 0·0487 0·052 0·047	 0·66225	 0·071
Phenyl Iodide, C_6H_5I.	8 88	1·8482 1·7272	1·62755 1·58301	0·0444 0·0441 0·0450 0·0461 0·0465 0·0452	 0·54107	 0·083
Aniline, C_6H_7N	11·2 90·1	1·02792 0·95783	1·5912 1·54867	0·0490 0·0513 0·0546 0·0537 0·0538 0·0525	 0·97283	 0·054

Table II. (*continued*).

Substance.	Temp.	Density.	μ_D.	$\beta = \dfrac{(\mu-1)v-(\mu_1-1)v_1}{\mu-\mu_1}$	v at lower temp.	$\dfrac{\beta}{v}$.
Dimethylaniline, $C_8H_{11}N$.	8	0·96688	1·56535	0·0610		
	89·7	0·89961	1·52345	0·0665		
				0·0671		
				0·0850		
				0·068	1·03425	0·065
a-Naphthylamine, $C_{10}H_9N$.	51	1·10043	1·67084	0·060		
	88·4	1·07207	1·65209	0·0678		
				0·0704		
				0·0800		
				0·069	0·90873	0·076
Ethyl Cinnamate	12·9	1·05560	1·56351	0·060		
	91·1	0·98815	1·52500	0·0663		
				0·0684		
				0·080		
				0·068	0·94733	0·071
Acetyl-acetone	11	0·98506	1·44493	0·211		
	99·3	0·89787	1·39634	0·222		
				0·224		
				0·251		
				0·278		
				0·240	1·0152	0·235
Methyl-acetyl-acetone.	8·34	0·99189	1·44210	0·173		
	99·2	0·90324	1·39526	0·178		
				0·185		
				0·207		
				0·186	1·0081	0·185
Ethyl-acetone-oxalate.	17	1·12879	1·46503	0·0676		
	100	1·04109	1·42617	0·0700		
				0·0772		
				0·0760		
				0·0710	0·8859	0·080
Ethyl-diaceto-acetate.	17·6	1·09313	1·45729	0·0476		
	99·8	1·0675	1·41932	0·0479		
				0·0487		
				0·0530		
				0·0603		
				0·0515	0·9148	0·0564

Table II. (*continued*).

Substance.	Temp.	Density.	μ_D.	$\beta = \dfrac{(u-1)v - (\mu_1-1)v_1}{\mu - \mu_1}$.	v at lower temp.	$\dfrac{\beta}{v}$.
Diacetyl-acetone	60	1·04248	1·46691	0·292		
	99·8	1·00615	1·44386	0·291		
				0·309		
				0·350		
				0·314	0·96146	0·326
Allyl-acetyl-acetone ...	13·5	0·97671	1·46156	0·1515		
	99·2	0·89832	1·41868	0·1614		
				0·1680		
				0·1894		
				0·205		
				0·175	1·0238	0·1709

Tables I. and II. contain the results yielded by substances of very varied chemical types. It may be stated at once that, although the last six substances have been put in the Table, the discussion of the figures they yield will be deferred. It is known that they are of very exceptional character; for example, that they change in chemical constitution when heated, so that it is not strictly the same substance we are dealing with at the two temperatures given in the Table[*]. Excluding these compounds, the values of β are of a satisfactory order. They do not vary largely, the extreme values being 0·09 and 0·043, most of them lying between 0·065 and 0·045. That is to say, on the hypothesis which led to the calculation, the actual space filled by one gramme of the substance is about one twentieth of a cubic centimetre.

Column 7 shows the value of β/v, that is the ratio of the actual to the apparent volume of a liquid. The extremes are 0·15 and 0·054. If we exclude methylene di-iodide, a substance of exceptional density, the extremes are 0·09 and 0·054, and twelve out of the sixteen liquids lie between 0·076 and 0·054; the average value is 0·064.

These results are promising, both with regard to the absolute magnitude and the approach to similarity of value for the different liquids. This last fact was to be expected, for it is probable that ordinary liquids, under similar conditions of temperature and pressure, have volume constitutions of a fairly uniform type.

It may be objected that the average values obtained for β and β/v are much too small, seeing that other estimates of

[*] Compare Perkin, Chem. Soc. Journ. 1892, p. 840.

these quantities give much larger figures.   The ratio

$$\frac{\text{actual volume of molecules}}{\text{apparent volume of liquid}}$$

is generally estimated to be about 0·2 or 0·3; that is, about four times greater than the value now found by the new hypothesis.

To this objection it may be replied :—

1. Prof. Tait has expressed the opinion that " the estimates hitherto made can hardly be called even rough approximations. But probably the particle does not occupy so much as 5 per cent. of its share of the whole content "[*].   This estimate is not far from the 6 per cent. yielded by the foregoing calculations.

2. It will be suggested at a later stage that the expressions which give 0·2 or 0·3 for the ratio β/v probably measure, not the molecular volume itself, but that part of the apparent volume which may be called the molecular domain.

Postponing further consideration of this argument, we may inquire whether the value of β is dependent on the particular temperatures employed in the observations.   That is to say, presuming that it is a measure of molecular volume, does it show any change in value at higher or lower temperatures? Very few series of observations are accurate enough to stand the severe test imposed on them by an attempt to answer this question.   Of the few that seem suitable, I shall give two examples, taken from the work of Ketteler[†].   From these it will appear that the answer varies, carbon disulphide showing a constant value for β at different temperatures, while water gives a *diminishing* value as the temperature rises.

Carbon Disulphide, CS_2.

Temperature.	v.	μ_D.	β.	$(\mu-1)(v-\beta)$.
$-20\overset{\circ}{}$	0·75582	1·65950	0·0476	0·46879
-10	0·76442	1·65158	0·0476	0·46878
0	0·77314	1·64375	......	0·46874
10	0·78207	1·63593	0·046	0·46872
20	0·79131	1·62806	0·046	0·46873
30	0·80093	1·62004	0·0464	0·46871
40	0·85515	1·61187	0·0459	0·46871

[*] Tait, 'Properties of Matter,' p. 90.
[†] *Ann. Phys. Chem.* xxxv. p. 693.

Here it is evident that the value of β remains practically constant through a range of 60° C. The values given were calculated from 0° as one of the temperatures in each case.

If β has the meaning here assigned to it, the above measurements indicate that 1 gram of carbon disulphide actually occupies 0·046 cubic centimetre. Moreover, if we take the ratio β/v, we find it to be 0·062 at 0° C., which is again very near the average value yielded by the many liquids already given.

<div align="center">Water.</div>

Temperature,	v.	μ_D.	β calculated from first.	β calculated for each pair.
20·9	1·00196	1·33287	......	
				·204
31·0	1·0044	1·33177	0·204	
				·114
56·0	1·0149	1·32776	0·150	
				·085
87·0	1·0336	1·32107	0·114	
				·067
94·0	1·0386	1·31943	0·108	

The result here is quite different from that shown by carbon disulphide; β varies with every change in the temperature. It is given in two columns, the first containing values obtained by taking each observation in conjunction with that at the lowest temperature. The next column contains values obtained by taking each pair of observations. This last series is the more suggestive.

1st. It shows β to be *diminishing* as the temperature rises, and gives the value it has between 87° and 94°. At this temperature, where the water is approaching its boiling-point, the value of β becomes 0·067 cubic centim., a close approximation to that given by the other liquids.

2nd. The ratio β/v at the high temperatures is 0·063, almost exactly the ratio 0·064 given by the other liquids.

These results are suggestive, and at once raise a question as to the meaning of the diminution in β as the temperature rises towards boiling-point. Any one acquainted with recent researches on the physical properties of liquids will at once recall those of Ramsay and Shields on Molecular Complexity; those of Thorpe and Rodger on Viscosity of Liquids, &c., as bearing on this question. The investigations mentioned, along with others, have rendered it almost certain that the molecule of water is a complex of the form nH_2O, and that the value of n in this expression diminishes as the temperature

rises. Consequently the high value now found for the volume of the water molecule, as measured by β, appears to be another indication of its greater molecular complexity, and the fall towards normal value as boiling-point is approached points to a molecular simplification as indicated by the other methods.

Somewhat similar, though more erratic, is the available evidence with regard to other liquids of known molecular complexity, such as the alcohols and acetic acid. The figures are not now quoted, as they must be redetermined with greater accuracy and perfect exclusion of atmospheric moisture during the experiments.

We may now test the value of β in another way. It has already been mentioned that the ordinary Gladstone expression fails to deal with the transition from liquid to gas, and the suggestion is now made that the discrepancy is due to the neglect of the volume of the particles, a quantity which practically vanishes in the case of vapours.

The question arises, will the value of β deduced from a liquid bring the liquid and gaseous numbers into agreement? Not many observations are available for this comparison. Obviously the same specimen ought to serve for the liquid and vapour. The work of Lorenz[*] and Prytz almost exhausts the published data of this sort.

Lorenz gives two observations on the liquid at different temperatures, and also an observation on the vapour formed by the liquid. Unfortunately Lorenz selected the temperatures of 10° and 20° C. for the observations on the liquids, which are too near one another to afford a very satisfactory basis for calculating β. Notwithstanding this, the results as shown in the following table are very encouraging.

Substance.	Temp.	Specific Refraction $(\mu-1)v$.		β calculated from Liquid.	Specific Refraction $(\mu-1)(v-\beta)$.	
		Liquid.	Vapour.		Liquid.	Vapour.
Carbon Disulphide ...	10	·4889	} ·4289	0·0886	·4334	·4289
,, ,, ...	20	·4882				
Chloroform ,,..........	10	·2979	} ·2681	0·0672	·2677	·2681
,, ...	20	·2975				
Ethyl Iodide..........	10	·2634	} ·2334	0·0685	·2282	·2334
,, ,, ...	20	·2629				
Ethyl Acetate	10	·4148	} ·401	0·030	·4035	·401
,, ,, ...	20	·4147				
Ethyl Ether	10	·4905	} ·4561	0·098	·4554	·4561
,, ,, ...	20	·4900				

* Wied. *Ann.* 1880.

This table shows that the difference between the specific refraction of a liquid and its vapour as calculated by the Gladstone expression may be 10 per cent. of the whole; also that if the value of β as calculated from the liquid be employed in the modification now proposed, the difference between the liquid and vapour falls to less than 1 per cent. With a more accurate estimate of β this difference might be still further reduced. The modified expression gives practically a constant for both liquid and vapour.

One remark ought to be made. The value of β for carbon disulphide is much greater than that deduced from Ketteler's figures already quoted; a fact which is difficult to explain, though difference of specimen may have something to do with it.

There is another set of observations by which β can be tested. Prytz has given data for nine liquids and their vapours; but as he only took one observation on the liquid his work is only available for calculating β from the liquid and vapour values. This can be compared with the average values previously obtained.

Substance.	β calculated from Liquid and Gas.
Methyl Alcohol	0·09
Ethylene Chloride	0·116
Ethedene ,, ...	0·085
Acetone	0·091
Methyl Acetate	0·0655
Ethyl Formate	0·093
Propyl Iodide	0·112
Methyl Propionate	0·096
Benzene.......................	0·16

These values are slightly higher than those deduced from two observations on the liquid, but the difference is not great.

A *prima facie* case having been shown for attaching some physical significance to the symbol β, it appeared probable that the values for different substances would show definite relationships between themselves; or that the value of β for a given substance would be related to the value of v at the freezing, boiling, or critical temperature.

Of these the boiling-point is the one for which data are mostly available, and a little examination suggested a close relation between the absolute temperature of the boiling-point and the two volumes v and β. It may conveniently be written

$$\beta \propto \frac{v_T}{\sqrt{T}}.$$

For the Centigrade scale the relation indicated seems to approach one of equality.

There are ten substances for which β, v_T, and T are known with sufficient (or apparently sufficient) accuracy. The above equation is here used to find the value of β from v and T, and the value so obtained is compared with that given by the optical data.

The following table shows that the results are in fair agreement, if we remember that the three data compared together are mostly due to different observers using different specimens.

Substance.	v_T.	$\sqrt{\bar{T}}$.	$v_T \div \sqrt{\bar{T}}$	β from refraction.
Heptane	1·629	19·3	0·084	0·081
Carbon Disulphide ...	0·818	17·89	0·0457	0·0460
Aniline	1·146	21·2	0·054	0·0525
Toluene	1·282	19 62	0·065	0·068
Water	1·043	19·34	0·054	$\left\{ \begin{array}{l} 0\cdot067 \\ 0\cdot060 \end{array} \right.$?
Phenyl Chloride	1·044	20·1	0·052	0·054
Phenyl Bromide	0·766	20·7	0·0365	0·047
Phenyl Iodide	0·6388	21·5	0·03	0·045
Ethyl Cinnamate	1·2005	23·15	0·052	0·068
Ethylene Dibromide...	0·5178	20·13	0 026	0·031

Many other figures might be given but they are of inferior accuracy, and ought not to be placed along with those just quoted. The examples are sufficient to establish a case for further inquiry, inasmuch as the agreement is close enough in six or seven cases to preclude the notion of accidental coincidence.

If additional data confirm the foregoing result, it affords us another method of calculating the quantity β when the boiling-point and the density at that temperature are known. I propose to get β for other substances by this method, and test several deductions by the result. It is evident, on general grounds, that values of β calculated by this method will be of the same order of magnitude as that given by the optical data. All ordinary liquids boil between, say, 50° and 300° Centigrade, or 320° and 470° absolute ; and the square roots range between 18 and 22, with average about 19, which is fairly near the average ratio for v_1/β.

It is hardly necessary to point out that this relation may possibly supply a hint as to the unknown law between volume-relationships of liquids and the temperatures. For example, I was tempted to compare the varying value of β in the case of water with its very varied coefficient of thermal expansion α.

Apparently, these two quantities are inversely proportional as shown in the following table by the comparative constancy of the product $\beta \times \alpha$.

Water.

Temperature-range.	β.	α.	$\beta \times \alpha$.
$20°9$ to $3°1$	0·203	·00025	·0000505
31 „ 56	0·144	·0004	·0000576
56 „ 87	0·082	·00059	·0000482
87 „ 94	0·067	·00072	·0000482

In reading this table the approximate character of the value for β must be kept in mind. The last column then indicates the probability of some connexion between β and α. α is calculated from data given by Thorpe.

Slight though this evidence may appear it seems to me to warrant further careful investigation, in view of the desirability of finding some method of obtaining a general law governing the thermal expansion of liquids, and the admitted difficulty of the problem.

Note.—I have quite recently calculated the value of β from another series of figures due to Ketteler, and quoted in Landolt and Bornstein's tables. The general tendency is as above, but the product $\beta \times \alpha$ varies from ·$0_4$428 to ·$0_4$600. There is perhaps internal evidence, however, for regarding the figures as less accurate than the foregoing, so that I let the matter stand, subject to correction.

Summing up the general results obtained so far, we find:—

1. In simple liquids the quantity β lies between narrow limits, the average being 0·05 cubic centim.
2. The ratio β/v averages 0·064. That is, the actual volume of the molecules is about 6 per cent. of the apparent volume.
3. Liquids known to have exceptional physical properties, such as water &c., give higher values of β than usual. This higher value changes with temperature, and is probably a measure of molecular complexity.
4. There is reason to think that some liquids, like carbon disulphide, yield a constant value for β at different temperatures.

5. The value of β given by a liquid enables us to apply the Gladstone formula (amended) during the transition from the liquid to the gaseous state.

6. There are grounds for believing that the value of β is related to other volume-relationships of the substance, as, for example, the specific volume at the boiling-point.

7. In some cases there may be a connexion between β and the coefficient of thermal expansion.

A further argument for the introduction of the quantity β is the fact that it will remove certain anomalies in molecular refractions, bringing the value for hydrogen, chlorine, &c. into harmony with that given by the gaseous elements. This point, together with others of a like nature, is reserved for another paper.

So far as the suggestions thrown out are probable, it would appear that "the actual volume of the particles" is not a correct expression for β. In the case of water, β has a varying value, which is attributed to the resolution of its complex molecule into simpler forms. But such resolution could not diminish the volume of the particles, unless we mean by this phrase "the true volume of the atoms + the inter-atomic space." If we imagine a surface drawn to enclose the molecule, it will include such space as lies between the atoms in that molecule. Similarly, when two molecules coalesce to form one of greater complexity the space occupied by the two is greater than before. They do not actually touch, so that the enclosing surface has a greater volume than twice that which encloses one molecule.

The results obtained so far show that the modified Gladstone expression promises to cover all ranges of density[*]. This wide range of applicability is obtained by emphasizing the volume-relationships involved in the formula—a fact which acquires further significance when we remember that it is as a measure of a volume that the Gladstone expression has proved so useful. For the specific refraction of a substance, $(\mu-1)v$, is evidently a fractional part of the specific volume v. Moreover, both Dufet (*Journ. de Phys.* 1885) and Sutherland (Phil. Mag. 1888), in developing a theoretical basis for the Gladstone law, have shown that "volume of molecules" is involved, though the exact definition of the phrase is not arrived at.

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[*] Except perhaps in the case of certain solids. See data for refraction of solids collected in the paper by Dr. Gladstone and myself already mentioned, Chem. Soc. Trans. 1895, p. 831.

It seemed worth while asking whether this fractional part of the volume had a physical meaning. If the quantity β may be regarded as a measure of true molecular volume, and there still remain a certain element of volume to be measured, it will most probably be found by accepting a well-known kinetic constitution for the liquids. If temperature be constant, we may assume that each molecule of a liquid vibrates as a whole over a certain region called its domain, the centre of this region being defined as the centre of the molecule when in its mean position.

The extent of the domain, and the relation between it and the total volume, will depend on the energy of molecular motion, and on the law of molecular force with regard to distance.

Thus the apparent volume is made up of fractional parts, one of which may be called the sum of the volumes of the molecules, another the sum of the volumes of the domains, and a third the interstitial spaces. A satisfactory theory for evaluating these can perhaps not be found till more is known of the magnitude and law of the molecular forces, but an empirical examination suggested that $(\mu-1)v$ might possibly serve as a basis for finding the domain. At any rate it gives by transposition a part of v which fairly answers to the only criterion of the domain which I can lay down.

Nothing is known as to possible change of the dimensions of the molecules themselves, but it seems highly probable that the domain of a given substance will most certainly differ under different physical conditions. Still further does it seem probable that the domain of different substances, heated between the same temperature-limits, may change in the same ratio. Figures in the tables which follow will prove this for the new expression, to what may be called a first approximation.

The transformation referred to is

$$(\mu-1)v=\mu\left[v-\frac{v}{\mu}\right],$$

the value of the square bracket on the right being equal to $\frac{\mu-1}{\mu}.v.$

It was evident to me, and will be to any one familiar with the data given by molecular refractions, that this last expression gives a fraction of v tolerably near that obtained by the use of the other well-known expression

$$\frac{\mu^2-1}{\mu^2+2}.v.$$

I can best illustrate this by taking a table from a lecture on the "Range of Molecular Forces" delivered to the Chemical Society by Rücker (Chem. Soc. Journ. 1888, p. 253).

Using Hopkinson's data, Rücker compares the values of

$$\frac{K-1}{K+2} \quad \text{and} \quad \frac{\mu^2-1}{\mu^2+2}$$

for five substances (K = specific inductive capacity). His object is to show that the figures justify well-known theories due to Clausius, Clerk-Maxwell, and others. Assumptions underlying these expressions make them a measure of the ratio

$$\frac{\text{true volume of molecules}}{\text{apparent volume of liquid}},$$

though the expression "true volume of molecules" is a quantity depending on what is better known as the "diameter of the molecule," *i. e.* the smallest distance between the centres of molecules.

The table is quoted bodily, with an additional column to show the value of $\dfrac{\mu-1}{\mu}$, this last being the factor of v in the square bracket of the transposed expression.

Substance.	Formula.	K.	μ^2.	$\frac{K-1}{K+2}$.	$\frac{\mu^2-1}{\mu^2+2}$.	$\frac{\mu-1}{\mu}$.
Amylene	C_5H_{10}.	2·05	1·9044	0·260	0·232	0·245
Benzol	C_6H_6.	2·38	2·2614	0·315	0·296	0·334
Toluol	C_7H_8.	2·42	2·2470	0·321	0·291	0·333
Xylol............	C_8H_{10}.	2·39	2·2238	0·317	0·290	0·329
Cymol	$C_{10}H_{12}$.	2·25	2·2254	0·294	0·290	0·295

Here it is evident that there is a close agreement among the three sets of figures, amply sufficient to justify further examination. So far as differences occur, $\dfrac{\mu-1}{\mu}$ is nearer $\dfrac{K-1}{K+2}$ than is $\dfrac{\mu^2-1}{\mu^2+2}$.

In pursuing this comparison I shall introduce β, so that

$$(\mu-1)(v-\beta) = \mu\left[(v-\beta) - \frac{v-\beta}{\mu}\right].$$

The square bracket is equal to

$$\frac{\mu-1}{\mu}(v-\beta),$$

and it is under this head that the figures appear in the following tables :—

Carbon Disulphide.

Temperature.	$\frac{\mu^2-1}{\mu^2+2}.v.$	$\frac{\mu-1}{\mu}.(v-\beta).$	$\frac{v-\beta}{\mu}.$	$\frac{v-\beta}{\mu}$ calculated.
-20	0·2788	0·2821	0·4277	0·4259
-10	0·2793	0·2835	0·4349	0·4341
0	0·2798	0·2847	0·4424	0
10	0·2803	0·2867	0·4494	0·4502
20	0·2808	0·2875	0·4578	0·4581
30	0·2813	0·2890	0·4659	0·4659
40	0·2819	0·2904	0·4746	0·4735

The experimental data are Ketteler's, and have already been given.

On comparing columns 2 and 3, it is seen that the figures are remarkably close to one another. The difference is just over 1 per cent. at $-20°$, and though it increases as the temperature rises, it only just exceeds 3 per cent. at $+40°$ C.

Column 4 contains the values of the second term in the bracket, or $\frac{1}{\mu}$th of $v-\beta$; and column 5 contains the "calculated" values for the same expression. The calculation is made by taking the value at $0°$ C. and multiplying by the square root of the ratio of absolute temperatures. Thus the value at $-20°$ is equal to

$$0·4424 \times \sqrt{\frac{254}{274}} = 0·4259.$$

I was led to try this by the results obtained in the first part of the present paper, and the extremely close approximation of the calculated to the other numbers is surely of some importance. The quantity $\frac{v-\beta}{\mu}$ will be referred to as the interstitial space.

The next table contains data for substances already mentioned.

Substance.	Temp.	$\dfrac{\mu-1}{\mu}(v-\beta)$.	$\dfrac{\mu^2-1}{\mu^2+2}v$.	Difference.		Ratio of New Values.
				Actual.	per cent.	
Thymol	24·4	0·39022	0·3110	0·079	20	} 1·0154
	77	0·39542	0·3124	...	...	
Cinnamic Alcohol......	24·8	0·3208	0·3168	0·004	1·2	} 1·0152
	77	0·3261	0·3182	...	...	
Anethol	14 9	0·3378	0·3241	0·0137	4	} 1·0199
	77	0·3445	0·3260	...	...	
a-Methyl a-Naphthol	14	0·3255	0·3182	0·007	2	} 1·0187
,, ,,	77	0·3316	0·3202	...	...	
Dimethyl Naphthalene	16	0·3377	0·3395	−0·0018	−0·6	
	78	0·3438	0·3412			
Heptane..................	12	0·3853	0·3451	0·04	10	} 1·030
	89	0·3968	0·3471	...	...	
Octyl Iodide	14	0·2303	0·2164	0·014	6	} 1·024
,, ...	88	0·2358	0·2177	...	−11	
Methylene Iodide......	8	0·1091	0·1216	−0·012	...	} 1·0318
,, ...	87	0·1126	0·1225	...	...	
Toluene	10·7	0·3591	0·3376	0·021	6	} 1·0312
,, ...	90·3	0·3703	0 3403	...	...	
Phenyl Chloride	9·6	0·2922	0·2771	0·015	5	} 1·029
,, ...	89	0·3007	0·2793	...	...	
Phenyl Bromide	4·2	0·2230	0·2168	0·006	3	} 1·031
,, ...	89·2	0·2296	0·2185	...	...	
Phenyl Iodide	8	0·1913	0·1919	−0·0006	−0·3	} 1·028
,, ...	88	0·1967	0·1935	...	...	
Aniline	11·2	0·3417	0·3288	0·013	4	} 1 0273
,, ...	90·1	0·3511	0·3319	...	...	
Dimethylaniline	8	0·3462	0 3336	0·0126	3·6	} 1·0304
,, ...	89·7	0·3567	0·3363	...	...	
Ethyl Cinnamate	12·9	0·3169	0·4210	0·104	33	} 1·0255
,,	91·1	0·3250	0·4378	...	...	
a-Naphthylamine	51	0·3370	0·3396	−0·0026	0·8	{
,, ...	88·4	0·3408	0·3409	...	...	
Acetyl-acetone	11	0·2387	0·2702	0·0315	13	} 1·0349
,, ...	99·3	0·2488	0·2678	...	...	
Methyl-acetyl-acetone	8·34	0·2560	0·2668	−0·0108	4	} 1·033
,, ...	99·2	0·2800	0·2656	...	...	
Ethyl-acetyl-acetone...	15·4					
,, ...	100·3					
Ethyl-acetone-oxalate	17·0	0·2587	0·2449	0·0138	5	} 1·0272
,,	100·0	0·2665	0·2545	...	...	
Ethyl-diacetol-acetate	17 6	0·2710	0·2493	0·0217	8	} 1·0267
,,	99·8	0·2615	0·2367	...	...	
Diacetyl-acetone	60·0	0·2065	0·2667	−0·0602	29	{
,, ...	99·8	0·2089	0·2639	...	...	
Allyl-acetyl-acetone ...	13·5	0·2681	0·2812	−0·0131	5	} 1·0322
	99·2	0·2769	0·2809	...	...	
Ethyl Acetate	10	0·2909	0·2546	0·0363	12	} 1·0039
,, ...	20	0·2920	0·2549	...	...	
Chloroform	10	0·1848	0·1990	0·0058	3	} 1·0040
,, ...	20	0·1855	0·1791	...	...	
Ethyl Alcohol	10	0·3266	0·2804	0·046	14	} 1·0029
,, ...	20	0·3276	0·2807	...	...	
Ethyl Iodide	10	0·1514	0·1557	−0·0043	3	} 1·0046
,, ...	20	0·1521	0·1558	...	...	
Carbon Disulphide ...	10	0·2668	0·2805	−0·013	5	} 1·0049
,, ...	20	0·2681	0·2809	...	...	

On examining this table we find that the new expression gives results which very fairly agree with those derived from Lorentz's formula.   The average difference between the two is about 5 per cent., a difference not greater than that which would be yielded by the expressions of Clausius and Maxwell. So far as this agreement goes we may regard

$$\frac{\mu-1}{\mu}(v-\beta)$$

as a fair approximation to a volume quantity, which I may be allowed to call " molecular domain."

The value, as given by either formula, increases with the temperature.   The highest increase by the μ^2 expression is about one per cent. in the case of aniline.   Whether such an increase could be attributed to the molecule proper, is an unsolved problem.   It is usual to regard the values yielded by the Lorentz formula as more constant than here appears, but the figures are too numerous and too reliable to leave any doubt about the magnitude of the change.

As I have already said, it seems probable that domains will change in the same ratio between the same temperature limits. This can be tested for the new expression by the figures in the last column, which gives the ratio of the two values for

$$(v-\beta)-\frac{v-\beta}{\mu}\ \text{ or }\ \frac{\mu-1}{\mu}(v-\beta)$$

found at two temperatures.

To facilitate comparison, the substances are arranged in groups, marked off by a line.   The members of each group are heated between approximately the same temperatures.   Thus thymol is heated between $24°\!\cdot\!4$ and $77°$, cinnamic alcohol between $24°\!\cdot\!8$ and $77°$.   The domain of the first increases in the ratio $1\!\cdot\!0154$, that of the second in the ratio $1\!\cdot\!0152$.

The members of the large group beginning with heptane and ending with ethyl cinnamate are heated between limits the lower of which lies between $4°$ and $12°$, while the upper limit lies between $87°$ and $90°$.   The new domain rises generally in this group by 3 per cent.   Out of the ten substances, seven give a ratio of increase very near to $1\!\cdot\!030$, the other three are near $1\!\cdot\!027$.

The next group includes eight substances heated between, say, $12°$ and $100°$.   Three give ratios close to $1\!\cdot\!033$, two yield $1\!\cdot\!027$.   The last group is heated from $10°$ to $20°$ only, and gives ratios close to $1\!\cdot\!004$, except in the case of alcohol.

These results seem to afford a reasonable presumption in favour of the figures being regarded as a measure of domain. There is evidently a tendency for the ratio of increase to be the same for the different liquids, although their densities vary

in the ratio of 5 to 1.   It is surely improbable that molecules of very varying atomic structure should have the same temperature increase, but the same improbability does not attach to "domain."

There is, however, one aspect of this question which may prove to be still more important.   It may be objected that the empirical* expression here used for obtaining the domain is too fanciful to be regarded with serious consideration.   It may further be pointed out that it is equivalent to

$$(\mu - 1)(v - \beta) \times \frac{1}{\mu},$$

as we have seen, and that the first two factors give a constant. Any relationships like those just alluded to must therefore be dependent on a more or less common temperature function for the refractive index.

It is evident, apart from arithmetic error, that this must be so.   But such an objection, while having weight against an expression obtained by the method we have pursued, at once raises a very suggestive question.   Does the evidence really justify the idea that the refractive indices of various substances change in the same ratio between the same temperature limits?   In other words, is the ratio magnitude of the change independent of the nature of the liquid?   The following table gives the evidence available.   The substances quoted are those already dealt with, but the comparison deals directly with the refractive indices, and is therefore free from all objections which might be urged against the hypothesis of this paper.

To facilitate comparison, the substances are again divided into groups, the order being slightly different from that previously given.   The refractive indices are given in column 3 ;

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* In the June number of the Chem. Soc. Journal appears an abstract of a paper by W. F. Edwards (American Chem. Journ.), who obtains the expression now proposed, as a new formula for specific refraction, thus :—
If V and V_1 are the velocities of light in space and the substance respectively, $\mu = \dfrac{V}{V_1}$.   Let $A = V - V_1$, then $A = \dfrac{\mu - 1}{\mu} V$.   If the difference A is proportional to the amount of substance, and assuming as unit one gramme of substance in 1 cub. centim., and that X is the retardation of velocity for unit substance, then

$$X = \frac{\mu - 1}{\mu} V \times \frac{1}{d}.$$

This is the same expression as that I propose for domain, multiplied by V.   As will be seen from my tables, and as Edwards shows, the value of X is not a constant.   It cannot therefore serve as a measure for specific refraction unless under stated conditions of temperature.   He promises to return to this, but will, I believe, only find the solution by substituting "volume of domain" for volume of substance.   As will be seen, I obtain his expression by a transformation of the Gladstone expression.

column 4 gives the ratio of the two indices, which are slightly corrected in column 5. This is done by calculating from columns 2 and 3 the average change in the index per degree, as shown in column 6. The figure thus obtained is used to calculate the change of index for 80° exactly, which means an alteration of only a degree or two for most substances. The ratio in column 5 is calculated then for a common interval of 80°, and will be somewhat nearer the truth than the uncorrected ratio in column 4.

Column 7 gives the exponent of μ in the statement $\mu^x \propto \dfrac{1}{T}$, where T is the absolute temperature. It therefore equals

$$\log \frac{T_2}{T_1} \div \log \frac{\mu_1}{\mu_2}.$$

The ratio $\dfrac{\mu_1}{\mu_2}$ is about 1·03, so that the different powers of it do not vary so much.

Substance.	Temp.	μ.	$\dfrac{\mu_1}{\mu_2}$.	$\mu_1 \div \mu_2$ corrected	$\dfrac{\mu_1 - \mu_2}{T_2 - T_1}$.	$x = \log \dfrac{T_2}{T_1} \div \log \dfrac{\mu_1}{\mu_2}.$
Heptane..................	12°	1·3922	1·0297	1·0317	·000522	8·1
,, ...	89	1·35197				
Methylene Iodide......	8	1·74935	1·0321	1·0325	·000671	8·0
,, ...	87	1·69500				
Toluene	10·7	1·5028	1·0316	1·0318	·000576	8·05
,, ...	90	1·45673				
Phenyl Chloride	9·6	1·53103	1·0293	1·0295	·000546	8·84
,, ...	89·2	1·48731				
Acetyl-acetone	11	1·44493	1·0349	1·0314	·000552	7·92
,, ...	99·3	1·39634				
Methyl-acetyl-acetone	8·34	1·4421	1·0334	1·0295	·000514	8·49
,,	99·2	1·39526				
Ethyl-acetyl-acetone...	15·4	1·44066	1·0324	1·0307	·000535	8·0
,, ...	100·3	1·3952				
Phenyl Bromide	4·2	1·56845	1·0303	1·0285	·000543	9·46
,, ...	89·2	1·52235				
Phenyl Iodide	8	1·62755	1·0279	1·0279	·000557	9·17
,, ...	88	1·58301				
Aniline	11·2	1·5912	1·0274	1·0278	·000538	9·23
,, ...	90·1	1·5487				
Dimethylaniline	8	1·5583	1·0270	1·0265	·000510	9·6
,, ...	89·7	1·51704				
Ethyl-acetone-oxalate	17	1·46503	1·0272	1·0262	·000536	9·35
,, ...	100	1·4263				
Ethyl-diaceto-acetate	17·6	1·4573	1·0270	1·0261	·000463	9·29
,, ...	99·8	1·4193				
Ethyl Cinnamate	12·9	1·5479	1·0253	1·0259	·000476	9·93
,, ...	91·1	1·5108				
Octyl Iodide	14·5	1·4922	1·0236	1·0254	·000463	9·99
,, ...	88·5	1·4579				
Thymol..................	24	1·5145	1·0154	1·0154	·000427	10·7
,, ...	77·3	1·4919				
Cinnamic Alcohol......	24·8	1·5731	1·0153	1·0153	·000447	10·6
,, ...	77·3	1·5494				

An examination of this table will show that for the same temperature limits there is a fair approach to constancy in the ratio $\frac{\mu_1}{\mu_2}$.

Thus the indices of the first seven substances all give ratios very near to 1·031. This is specially striking if we take particular cases like the first two on the list—heptane and methylene di-iodide—as shown in the following short table :—

	Temp.	Density.	Between the same temp. limit.	
			Ratio of Densities.	Ratio of Indices.
Heptane	12°	0·6903	1·11	1·0317
„	89	0·6230		
Methyl Di-iodide.....	8	3·348	1·07	1·0325
„ „	87	3·139		

It is also noteworthy that this same ratio (1·03) holds good in the case of those substances whose tendency to tautomerism is productive of anomalies. These are acetyl-acetone, methyl-acetyl-acetone, and ethyl-acetyl-acetone, which give abnormal values for β, and which differ from all other substances, even when tested by the Lorentz formula. Of course the ratio 1·03 is not preserved all the way down this group ; the lower members fall to about 1·026. Whether this means only a slight departure from the other value, or whether it indicates a breakdown of the suggested constant relationship can only be decided when many more accurate temperature observations are obtainable. The ratio altogether breaks down in the case of such substances as water, which, as I have suggested, show special relations to refractive index by reason of varying molecular complexity.

The last column in the foregoing table gives the ratio of the logarithms of temperatures and indices. Further research may make this column more valuable than it now appears.

Taken altogether, the table affords ground for believing that there are close relationships between refractive index and temperature, and, further, that the ratio of change for a particular temperature interval may be the same for many different liquids.

The question then arises, whether this last relation is direct, or arises from some material property changing with the temperature? Is it possible that the velocity of light may vary with temperature, apart from any relation to material substances, or is the foregoing relationship dependent upon some molecular function like that suggested, that is "molecular domain?"

It seems impossible to answer the first part of this question. The second part can be judged by analogy, which would appear to suggest that a molecular function is more probable. Thus, one might expect that the kinetic energy of the particles is the property directly increased by rise of temperature, and that many or all other properties of the molecule are consequential upon that. The apparent volume of course increases. That fraction of the volume which is measured by

$$\frac{\mu^2 - 1}{\mu^2 + 2} v, \quad \text{or} \quad \frac{\mu - 1}{\mu} (v - \beta)$$

also increases, whatever it may be called. This constant fact appears to be a decided argument in favour of these expressions, giving "domain" and not "volume of matter" simply. But again, if the plea for "domain" be granted, there ought to be increase, not only when the liquid is heated, but also when it is changed into a vapour. This is actually the case for $\frac{\mu - 1}{\mu} (v - \beta)$, the value of which increases in the ratio 1 to 1·4 or 1·5. This variability may be compared with that found by van der Waals for his constant b" ("Continuity &c.", Phys. Soc. translation, p. 409).

XXIX. *On the Changes in Length produced in Iron Wires by Magnetization.* By Louis Trenchard More, *Ph.D., Johns Hopkins University* [*].

THIS investigation was undertaken at the suggestion of Professor Rowland, and has for its object the finding of a relation between the change of length produced in iron wires by magnetization and the intensity of magnetization existing in the wire. It was hoped thus to obtain results that would be comparable and to avoid certain errors common to all previous work.

Historical.

That magnetizing an iron rod causes it to alter its length was first discussed by Joule[*] in 1847. His attention was called to the phenomenon by a machinist of Manchester, who imagined that the volume of a mass of iron was increased by magnetizing it. Joule, to test the opinion of the machinist, immersed a mass of iron in a closed vessel full of water in which stood a fine capillary tube. When the iron was strongly magnetized the height of the column of water in the tube remained unaltered, showing that within the limits of accuracy of his apparatus, for the intensity employed, the volume of the iron was unchanged. Bidwell[†] has also investigated this subject and found, on the contrary, that the volume was affected by magnetization. The volume diminishes at first and attains a minimum. It then increases, until with sufficiently intense fields the original size is regained. After reaching this point the volume continues to increase. As a consequence of this relation, if Joule had used an intensity either greater or less, he probably would have noticed a change in the volume. Joule afterwards, by means of a system of levers, found that the length of a rod was increased by the magnetizing force, and gave as a result of his observations the following laws :—

1st. When soft iron rods are magnetized their length is increased, and the elongation is approximately proportional to the square of the magnetizing force.

2nd. Tension applied to the rod diminishes the elongating effect, and " In the case of a bar one foot long and one-quarter inch in diameter, a tensile force of about 600 pounds caused all the phenomena of changes of length to disappear."

3rd. "That the elongation is, for the same intensity of magnetism, greater in proportion to the softness of the metal. It is greatest of all in the well-annealed iron bars, and least in hardened steel. This circumstance appears to me to favour the hypothesis that the phenomena are produced by the attractions taking place between the magnetized particles of the bar; an hypothesis in perfect accordance with the law which I have pointed out," that the elongation was proportional to the square of the intensity of magnetization.

The first two laws pointed out by Joule have been often confirmed, but the third seems to rest on a single experiment, and until very recently there have been no published records,

[*] Phil. Mag. [3] vol. xxx. pp. 76 & 225.
[†] Proc. Roy. Soc. vol. lvi. p. 94.

that I have seen, bearing on the result found by Joule. Shelford Bidwell*, while investigating the subject, obtained results the converse of Joule's,—indicating that not only hardening but also annealing the iron diminished the elongating effect. He mentions one specimen that, when annealed, contracted in length instead of elongating upon the application of the feeblest magnetizing force.

Barrett† in 1870 discovered that nickel, when magnetized, contracts instead of elongating. Three years later A. M. Mayer‡ published an account of his experiments on this subject. His results, in the main, verified Joule's observations, with the exception of the action of hard steel. This discrepancy was shown some years later by Bidwell to follow from their different methods of experimenting. Joule applied a current of the same intensity but once, and both on making and breaking the circuit observed an elongation; while Mayer used specimens already permanently magnetized, and on observing the temporary magnetization found a contraction on making circuit and an elongation on breaking it.

Mayer also observed hysteretic effects; that is, the elongation due to a magnetizing force was less if the force had been reached by successively increasing values than it was if the current had been decreased from a maximum: the rod remaining slightly elongated after the magnetizing force had been removed: an effect analogous to the lagging of the induction behind the magnetizing force. Nagaoka§ has discussed this phenomenon in the article cited, and has obtained complicated curves showing the complete cycle of the hysteretic phenomena for both iron and nickel.

The experiments mentioned were limited to comparatively feeble fields. The work of finding the effects due to intense fields has been most thoroughly done by Shelford Bidwell‖, who has found that rods do not continue to elongate indefinitely with increasing strengths of field as the other investigators supposed, but that a maximum value is after a time reached. The rod then begins to shorten, and very intense fields produce an absolute contraction which approaches a limiting value asymptotically. He also experimented with rings of iron, and with rods of steel, nickel, manganese steel, cobalt, and bismuth.

* Proc. Roy. Soc. vol. lv. p. 228.
† 'Nature,' 1882.
‡ Phil. Mag. [4] vol. xlvi. p. 179.
§ Phil. Mag. [5] vol. xxxvii. p. 131.
‖ Proc. Roy. Soc. vol. xxxviii. p. 265; vol. xl. pp. 109 & 237; vol. xlvii. p. 469; vol. lv. p. 228; Trans. Roy. Soc. vol. clxxix. (A), p. 205.

Investigations upon this subject have also been made by Berget[*], Nagaoka[†], Lochner[‡], Jones[§], and Bock[||].

For convenience I have collected in a summary the results obtained by the different observers.

Soft Iron.

Soft iron elongates when magnetized. The elongation attains a maximum, and then diminishes with increasing strength of field until a state is reached when the rod returns to its original length. Further increase of field causes the rod to contract.

There is no minimum length, the rod approaching asymptotically a limiting value.

For a given strength of field, both hardening and annealing diminish the elongation and increase the contraction shown by the rod before it was subjected to these operations (Bidwell).

Tension also diminishes the elongation and increases the contraction of the rod.

For a sufficiently great tension no elongation occurs, the rod contracting upon the application of the smallest magnetizing forces.

For a given length, the effects both of elongation and of contraction are greater for thin than for thick rods (Bidwell).

S. J. Lochner[¶] comes to the conclusion from his own experiments that the converse is true—that thick bars give greater expansion than thin ones.

Very little reliance can be put in these last experiments, and the dependence of the change of length upon the ratio of the length to the diameter cannot be inferred from them. Bidwell used three rods, 10 centimetres long and 2·65, 3·65, and 6·25 millimetres in diameter, and assumed them to be of iron of similar composition. It is well known that different specimens of iron, apparently similar in structure, give results that vary 25 per cent. and more. So that the small variations in the change of length noted by him cannot safely be said to be due to the differences in their diameters, especially as he made no determination of the permeability. Lochner avoided this error by testing an iron rod, and then, after having cut off a portion, testing it again. He, however, took no precautions to have the field uniform. His solenoid was nearly

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[*] *Compt. Rend.* tom. cxv. p. 722.
[†] Wied. *Ann.* liii. pp. 481 & 487 (1894).
[‡] Phil. Mag. vol. xxxvi. p. 504 (1893).
[§] Phil. Mag. vol. xxxix. p. 254 (1895).
[||] Wied. *Ann.* 1895.
[¶] Lochner, *loc cit.*

four times as long as the shortest rod used, and the ratio of the diameter to the length of the rod was only 1 to 32. Besides the uncertainties introduced by such a poor arrangement for a uniform field, great errors would be produced by the strong poles created at the ends of the rod.

Object of Experiment.

A careful study of the results obtained for iron by the different observers will show that although the general appearance of their curves is very similar, yet their absolute values vary widely, two specimens often having maximum elongations that differ 20 or 30 per cent. There is, unfortunately, no way of comparing these results, for it has been the custom to use as coordinates the change of length and the intensity of the external field. For a given apparatus this intensity depends only on the current used, and not at all on the specimen to be examined. The elongation is dependent upon the intensity of magnetization in the wire, and this is the quantity that varies with the specimen employed. For that reason the relation should be found between these two quantities.

It is of course essential to have the rod uniformly magnetized throughout its length; that is, the field should be uniform and there should be no free poles. These conditions may be best obtained in one of two ways : either by having the metal in the shape of a ring and observing the change in diameter of the ring when magnetized by a solenoid wound upon it, or by using long wires of the metal. In the second case only the middle part of the wire should be observed, and the solenoid used to magnetize it should be considerably longer than the portion of the wire experimented upon. In this investigation the latter method was chosen, as rings are less convenient and also because it was desirable to observe the effects of tension in the metal.

When a rod of iron is magnetized, the change in length observed is due to several causes—three at least; and to obtain a correct idea of the phenomena these causes and their effects should be separated. There is, first, the *direct action* of the magnetism, and this may possibly be due to the orienting of the magnetized particles of the rod. Secondly, there are indirect actions of the magnetism which tend to change the length of the rod. These indirect actions are the mechanical stresses created in the rod by the magnetism. The first of these mechanical stresses is the tractive force of the magnet, and is measured by $B^2/8\pi$. That this force exists, tending always to contract the rod, is seen from the fact that

if the magnet is cut in two the ends are held together by a force $B^2/8\pi$ per square centimetre, showing that this force must always be present when a rod is magnetized. The agreement between the theoretical value $B^2/8\pi$ and the experimental law for the lifting-power has been recently shown by E. Taylor Jones[*]. This effect for high intensities of magnetization is a large one, and becomes one of the most important factors in the observed changes in length. The second of these mechanical stresses is the effect due to the change in Young's Modulus when the rod is magnetized. That the elasticity is influenced by magnetization was shown theoretically by J. J. Thomson[†], and the phenomenon was observed last year in some experiments made by the writer ; but no quantitative results could be obtained beyond the fact that the elasticity for soft iron was slightly diminished. A. Bock[‡] concludes from his work that the decrease in elasticity must be less than one-half per cent. If the wire is not stretched by weights, this decrease in the elasticity will affect only the contraction due to the $B^2/8\pi$ force. This decrease in the elasticity, according to Bock, is very small and less than one-half per cent. On the other hand, if the wire is loaded with weights this effect becomes very marked since a large quantity, the stretch of the wire by the great weight, is altered. This question will be more fully discussed later in the paper.

If these two indirect actions were allowed for, there would remain only the direct action of the magnetism upon the metal under a constant tension. This latter relation would evidently furnish comparable results, and may in the future throw some light upon the action of magnetism on matter.

Apparatus.

Since it was necessary to obtain the modulus of elasticity for the specimen experimented on, in order to make a proper correction for the electromagnetic stress, and as I wished to observe the effects of mechanical stress, it was convenient to experiment on thin long wires of the metal placed in a vertical position. To magnify the phenomena, a system of levers was used involving the tilting of a mirror mounted on three legs very close together ; a method first invented by Professor Rowland. The general plan of using levers and a jacket cylinder was suggested to me by Dr. Ames.

The wire to be tested was suspended from a tall tripod

* Jones, *loc. cit.*
† 'Application of Dynamics to Physics and Chemistry,' p. 58.
‡ Bock, *loc. cit.*

standing on a stone slab that rested on two brick piers. A hole was cut in the slab so that the wire could be passed through it, and the free end permitted to almost reach the floor of the room. A hollow brass cylinder 1·6 centim. in diameter and about 68 centim. long (fig. 1) was screwed to

Fig. 1.

Fig. 2.
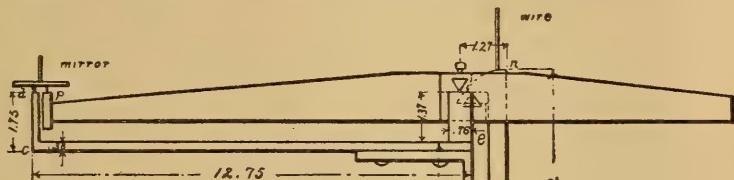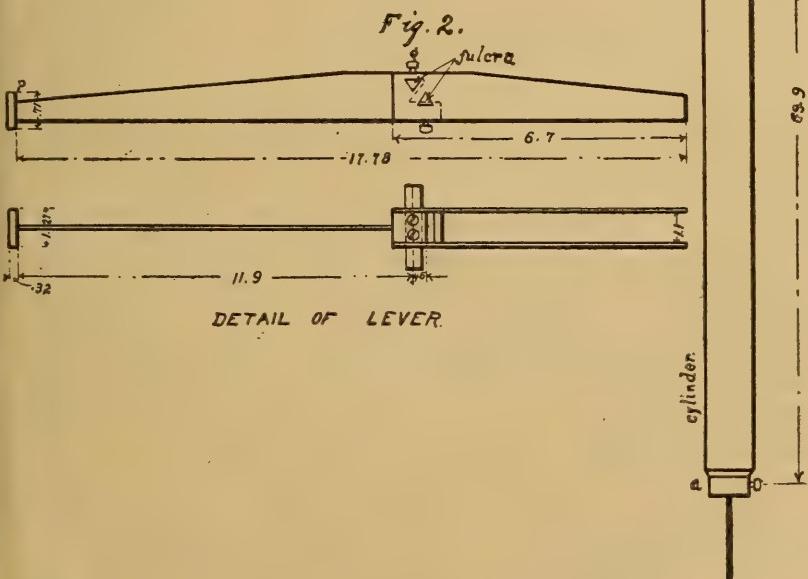
DETAIL OF LEVER.

the wire at a point a, a short distance above the stone slab ; a loosely fitting cork plug in its open upper end served to keep the wire in the axis of this cylinder. To the cylinder was screwed the brass arm $d\,e\,b$. At e was screwed a hard

steel support for the fulcrum of the lever. The side view of the support was of this shape ⌐___⌐, the two projections supporting the knife-edge, and the body of the lever passing between them. To keep the lever horizontal and to register changes of length, another knife-edge with its blade upwards was embedded in the lever. This knife-edge pressed against the piece $m\,n$ which was screwed to the wire at m. Now if the points m and a were separated or brought closer together, the knife-edges would no longer remain in a horizontal line and the lever would tilt. The end p of the lever, and the surface d of the arm $b\,e\,d$ were made planes to support a small brass table, having on its upper face a vertical plane mirror, and for legs three short bits of needles, two of which stood on p and one on d. By this arrangement the change in the length of $m\,a$ already magnified by the lever was much more apparent when the tilting of the mirror-table was read by means of a telescope and scale.

The most important dimensions are :—

Length of wire stretched, $m\,a$ . . . . 69·9 cm.
Ratio of lever arms . . . . . . 119/4·65
Distance between needle-points . . . 2·3 mm.
„ to telescope and scale . . 1660·0 „

The multiplying power of the apparatus was therefore

$$\frac{119}{4\cdot 65} \times \frac{1660}{2\cdot 3} \times 2 = 36941.$$

And as the scale was graduated to millimetres, one scale-division represented an actual change of length of $2\cdot 7 \times 10^{-5}$ millimetres.

The coil to magnetize the wire stood on the stone slab, and was long enough to reach just below the arm $c\,e$, so that the part of the wire $m\,a$ experimented on was in a practically uniform field.

The principal dimensions of this coil were as follows :—

Length of coil . . . . 83·7 cm.
External diameter . . . . . . 6·3 „
Internal „ . . . . . . 3·6 „
Number of wire 18
Number of turns 3045
„ layers 7
„ turns per centim. . . 36·4
Resistance of coil . . . . . . 10·53 ohms.
Strength of field per ampère . . 45·74 C.G.S.
Maximum field . . . . 260·00 C.G.S.

The core of this coil was made of two co-axal brass cylinders fastened together by the end plates of the coil. The space between these two cylinders was filled with water, which proved to be an excellent way of retarding the heat-effects produced by the current.

Method.

I at first intended to measure the elongation and the corresponding induction simultaneously, but found this difficult, and so adopted a more convenient and apparently as accurate a method. This was to first measure the current used to produce a given intensity of magnetism and the consequent changes in length, and afterwards to get the relation between the strength of field and the intensity of magnetism in the iron, the apparatus in the meanwhile remaining untouched. As the laboratory is situated in the city, the work had to be done late at night after traffic had stopped, for, in spite of all the precautions that could be thought of, the shaking of the apparatus could not be prevented. For this reason the induction was not determined immediately after obtaining the elongation-curve, but was done the next morning. The induction was measured by the method of reversals*. The induction-coil used for this purpose consisted of 200 turns of number 36 wire wound in one layer on a paper cylinder slightly greater in diameter than the specimen. This little cylinder was slipped over the wire and fixed halfway between $a\,m$. The galvanometer was calibrated by means of a standard coil having a wooden core. The secondary of the standard coil also consisted of 200 turns of wire, which plan saved much computation. The intensity was then calculated by the formula $B = H + 4\pi I$. Knowing the change in length and the intensity of magnetization for any current, of course the relation between these two quantities could be easily plotted. The current was supplied by a battery of storage-cells, and the resistance was regulated by a slide-resistance of copper-sulphate.

Results.

My first results were obtained from a specimen of moderately soft commercial iron wire, 1 millim. in diameter. This wire was free from stress except that due to the jacket-cylinder screwed to it, which weighed 350 grams. The elongations given (Table I.) are those due to temporary magnetism, and each value is the mean of two or three readings which did not

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* Ewing, London Electrician, April 1894.

vary by more than one per cent. The current was applied suddenly, and as soon as a reading was taken the contact was broken. This operation was then repeated, the current being increased each time, and readings taken until the maximum current was reached. By this means temperature-effects which are relatively slow to act were avoided.

Fig. 3.
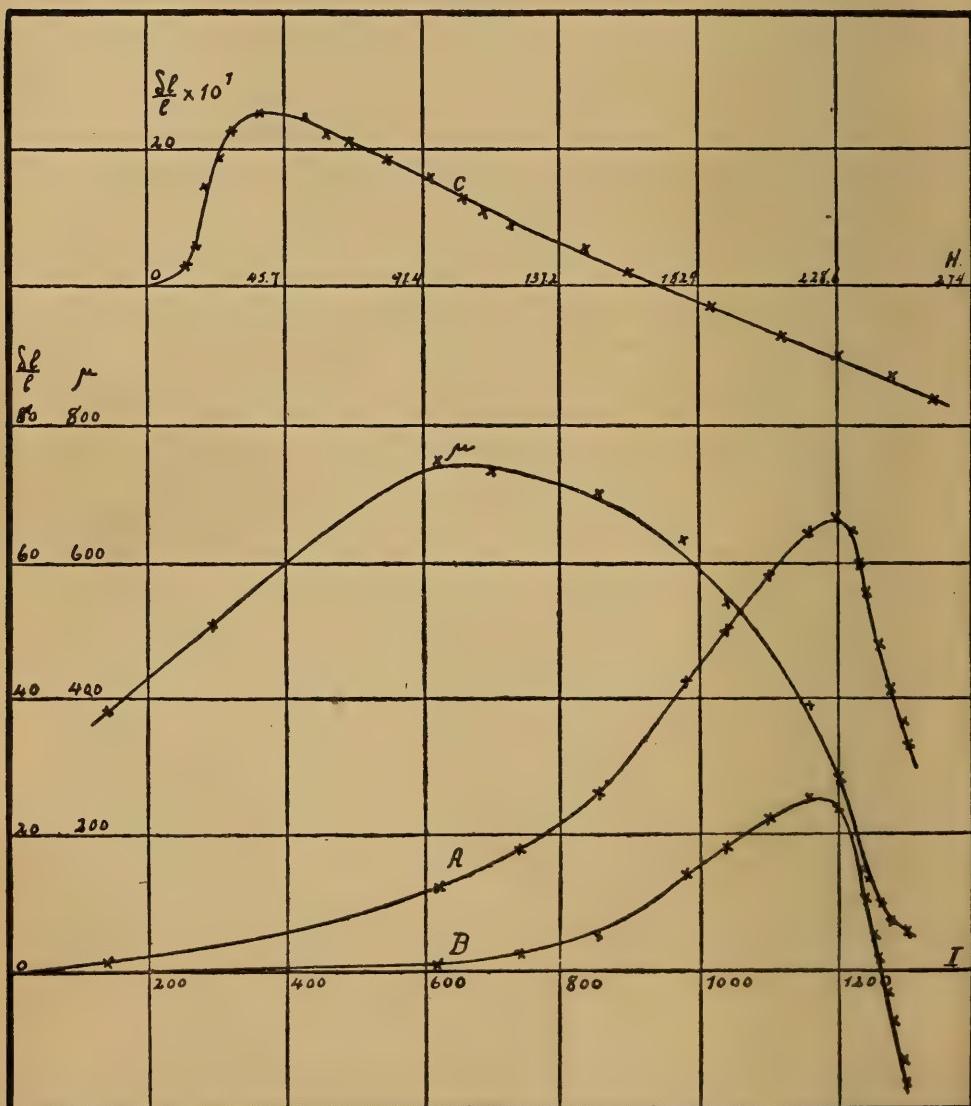
C.—Elongation and intensity of field.
B.—Elongation and magnetization.
A.—Do. corrected.

Fig. 3, C shows the relation between the elongation per unit length, $\dfrac{\delta l}{l} \times 10^7$, and the intensity of the field, H. This curve is seen to closely resemble in form those given by

Shelford Bidwell. When the relation is expressed between change of length and intensity of magnetization, the curve takes the very different form given by fig. 3, B. The wire slowly increases in length until an intensity of about 800 is reached. From that point until a maximum length is attained, at an intensity of 1200, the elongation is more marked. After reaching this maximum it rapidly contracts; the last portion of curve being approximately a nearly vertical straight line. The figure also shows that the point of maximum length does not correspond to the point of greatest permeability of the iron, as is seen by comparing this curve with the curve for permeability plotted on the same figure.

It is now necessary to make correction for the contraction due to the $B^2/8\pi$ force. This contraction is obtained from the formula $\dfrac{\delta l}{l} \times 10^7 = \dfrac{B^2/8\pi}{M}$, where M is the modulus of elasticity. My apparatus was well fitted for measuring the latter quantity. A weight of about five kilograms was hung on the wire and the elongations due to the additions of weights of 20, 50, and 100 grams were read. From these Young's Modulus was calculated in the usual manner. It was found to be $2 \cdot 2 \times 10^{12}$ for the specimen used. The contractions due to the $B^2/8\pi$ force were then calculated and are given in column 6 of Table I.

TABLE I.

H.	μ.	I.	B.	$\frac{\delta l}{l}$ (obs.).	$\frac{\delta l}{l}\left(\frac{B^2}{8\pi}\right)$.	$\frac{\delta l}{l}$ (corr.).
4·6	384·8	141	1770	+ 0·10	− 0·7	+ 0·80
7·3	507·0	294	3700	......	......	......
10·5	752·4	623	7900	1·16	11·3	12 46
11·8	733·0	700	8800	......	......	.... .
12·8	726·7	739	9300	2·71	15 65	18 33
15·5	695·0	856	10770	5·71	20·98	26·69
19·7	627·0	981	12350	14·71	27·60	42·31
24·2	541·4	1041	13100	18·78	31·05	49 83
28·8	482·7	1104	13900	22·92	34·95	57·87
37·6	389·1	1163	14630	25·55	38·53	64·13
53·0	286·3	1203	15170	24·78	41·69	66·47
60·4	253·7	1214	15320	23·23	42·47	65·70
67·7	227·7	1222	15410	21·30	42·96	64·26
80·0	193·8	1228	15500	18·74	43·46	62·20
93·3	167·2	1235	15600	15·49	44·02	59·51
103·8	150·8	1238	15650	12·81	44·30	57·11
111·6	140·7	1241	15700	11·03	44·59	55·62
121·2	130·0	1244	15750	9·20	44·88	54·08
145·4	109·6	1257	15930	5·42	45·90	51·32
159·1	100·6	1261	16010	+ 1·94	46 37	48·31
186·5	86·9	1274	16200	− 2·94	47·47	44·53
210·3	77·8	1281	16360	6·97	48·42	41·45
246·9	67·1	1299	16570	12·97	49·67	36·70
260·6	63·9	1304	16650	16·65	50·15	33·30

The last column of this table was found by taking the difference between the observed elongation and the $B^2/8\pi$ contraction. The relation between this corrected elongation, due to what has been called the direct action of the magnetism, and the intensity of magnetization is graphically shown by fig. 3, A. The effect of this correction is to make the elongation much greater for a given intensity. The maximum value of the elongation is more than twice as great as the observed maximum. And the greatest intensity employed, 1300 C.G.S. units, produces an elongation and not a contraction as observed.

No correction for the change in elasticity was made. For the present case it would be insignificant. See discussion of errors at end of this paper.

Effect of Hardening.

The effect of hardening the wire was next considered. A piece of the same quality of iron was heated to a bright red by passing a current through it, and then suddenly cooled. After the operation the wire was much harder and only slightly burnt on the surface. The observed changes in length, those due to $B^2/8\pi$, and the corrected values are given in Table II.

TABLE II.

H.	I.	B.	$\frac{\delta l}{l}$ (obs.).	$\frac{\delta l}{l}\left(\frac{B^2}{8\pi}\right)$.	$\frac{\delta l}{l}$ (corr.).
5·0	8	100	−0·00	−0·00	+0·00
8·7	53	670	0·05	0·08	0·03
12·8	272	3420	0·10	2·12	2·02
18·3	709	8920	0·20	14·41	14·21
27·4	923	11620	0·50	24·44	23·94
36·6	947	11940	0·70	25·77	25·07
45·7	1012	12770	1·85	29·48	27·63
57·2	1044	13180	3·10	31·42	28·32
68·5	1060	13390	4·10	32·42	28·32
96·5	1074	13600	7·40	33·43	26·03
118·8	1064	13490	5·40	32·93	27·53
138·5	1100	13560	(?) 15·00	35·24	20·24
180·1	1126	14320	24·20	37·11	12·91

Hardening the iron makes the elongation smaller, and for the present specimen, the least intensity of magnetization caused the wire to contract (fig. 4, B). The corrected relation between the change of length and the intensity is shown by fig. 4, B'. On this figure is also plotted curve A, the same relation, taken from fig. 3, for the wire when not hardened, and curve A' shows the corrected relations for the same.

Although the observed change for the hardened wire was a
contraction, the contraction due to the $B^2/8\pi$ force was suffi-
cient to bring the values above the zero axis.   So, again, the

Fig. 4.
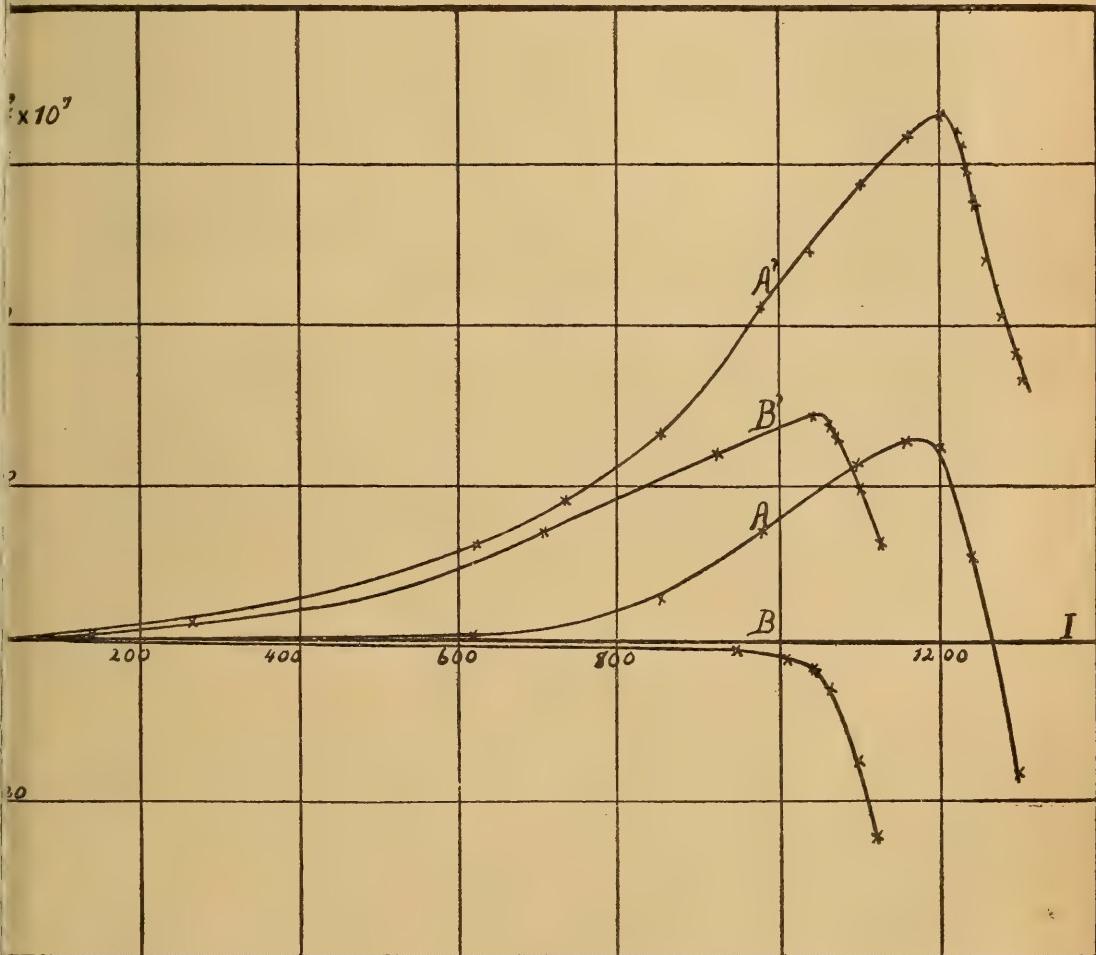
A.—Wire natural.   B.— Wire hardened.
A'.—Do. corrected.   B'.—Do. corrected.

direct action of the magnetization is to elongate the wire.
The corrected curve is very similar to the curve for the iron
in its original state.   The absolute values are, however, much
diminished and the maximum occurs, for the specimen, with
a less intensity.   The correction for the change of elasticity
can be neglected as in the first case.

Effect of Strain.

To find the effect of strain the wire was loaded with a
weight of 750 kilog. per square centimetre, and the relation

between the elongation and the intensity of magnetization obtained as in the previous cases. The wire was then loaded with a weight of 1750 kilog. per square centimetre and the same relations found. The values are given in Tables III. and IV. The effects of strains are also shown graphically by fig. 5, for the observed and corrected value. On consulting the figure, it is seen that straining the wire produces the the same change that hardening it does. The values are reduced, and the maximum points occur with less intense magnetization. The curves in this figure, as well as in the two former figures, marked no load, have an inaccuracy due to the strain caused by the weight of the jacket cylinder, and should have ordinates a trifle greater.

Although the change in elasticity has hitherto produced little effect, as soon as the wire is much strained this correction becomes very important and will modify the curves materially. This alteration in the curves it has not been possible to make, as the relation between the change in elasticity and the intensity of magnetization is unknown. However, from Bock's results some approximations may be arrived at, and these will be considered when the errors likely to occur in this investigation are discussed.

TABLE III.

H.	I.	B.	$\frac{\delta l}{l}$ (obs.).	$\frac{\delta l}{l}\left(\frac{B^2}{8\pi}\right)$.	$\frac{\delta l}{l}$ (corr.).
6·9	636	·8000	+0·12	−11·58	+11·70
11·4	918	11550	0·62	24·14	24·76
18·5	1080	13600	2·63	33·46	36·09
24·2	1109	13960	3·73	35·27	39·00
30·2	1139	14340	3·87	37·19	41·06
34·7	1150	14480	3·48	37·94	41·42
43·9	1167	14700	2·42	39·09	41·51
55·8	1184	14930	+1·20	40·33	41·53
73·2	1204	15200	−0·39	41·79	41·40
81·8	1212	15300	1·16	42·35	41·19
100·6	1223	15470	4·41	43·30	38·89
122·5	1235	15640	9·10	44·24	35·14
148·1	1247	15820	14·13	45·27	31·14
157·7	1253	15910	15·80	45·80	30·00
175·1	1265	16070	18·58	46·71	28·13
192·1	1276	16230	25·05	47·65	22·60
228·6	1287	16400	29·03	48·65	19·62
251·4	1293	16500	32·13	49·26	17·13

TABLE IV.

H.	I.	B.	$\frac{\delta l}{l}$ (obs.).	$\frac{\delta l}{l}\left(\frac{\mathrm{B}^2}{8\pi}\right).$	$\frac{\delta l}{l}$ (corr.).
5·5	581	7300	−0·19	− 9·64	+ 9·54
9·1	922	11600	0·58	24·35	23·77
13·7	1011	12720	1·26	29·27	28·01
21·5	1070	13470	2·90	32·83	29·93
27·4	1100	13860	4·06	34·76	30·70
36·6	1134	14280	5·90	36·89	30·99
45·7	1155	14560	7·36	38·36	31·00
54·9	1167	14710	9·68	39·14	29·46
73·2	1178	14880	13·84	40·05	26·21
86·9	1186	14990	16·64	40·65	24·01
96·0	1190	15050	19·74	40·97	21·23
111·1	1198	15160	23·63	41·58	17·95
128·0	1207	15290	27·87	42·29	14·42
139·4	1212	15370	32·51	42·74	10·23
150·9	1217	15440	33·97	43·12	9·15

Fig. 5.
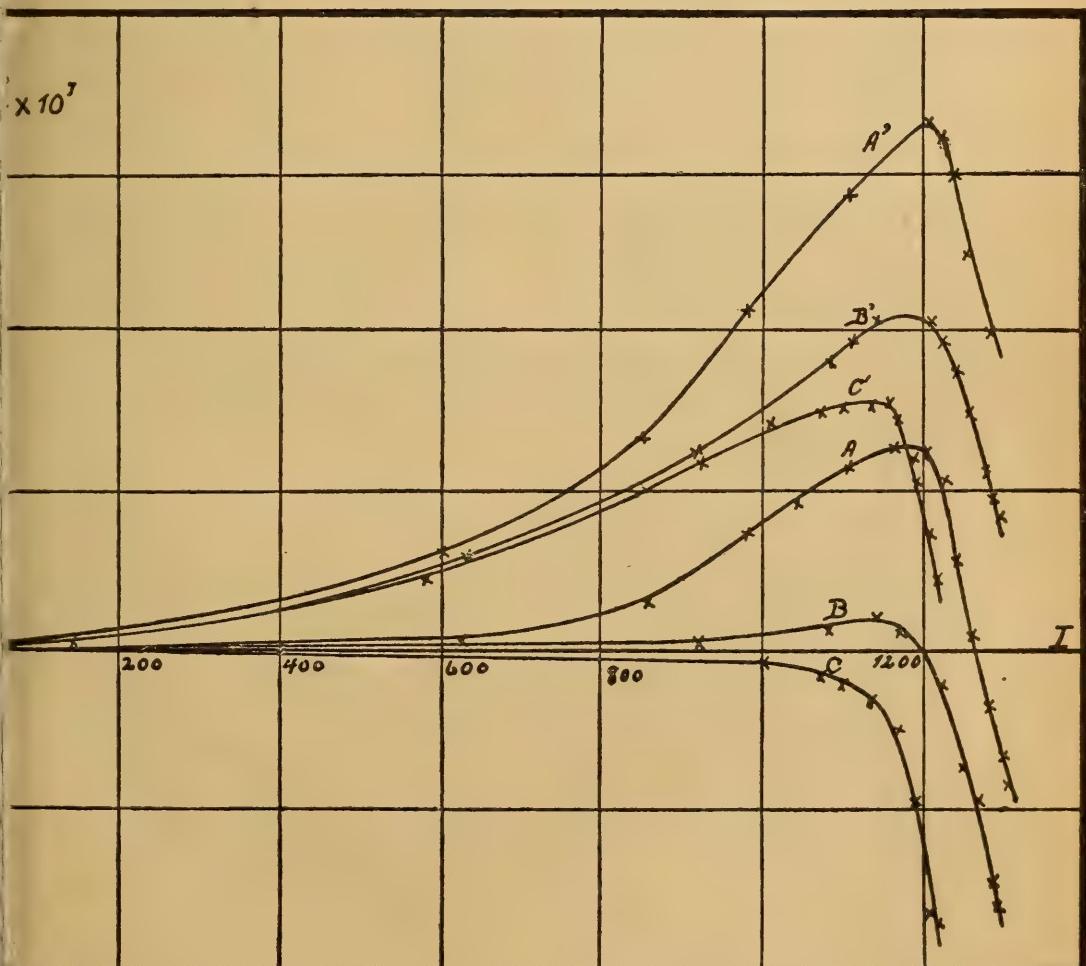
A.—No load.   B.—750 kgs. per sq. centim.   C.—1750 kgs. per sq. cm.
A'.—Do corrected.   B'.—Do. corrected.   C'.—Do. corrected.

Possible Errors.

It has been shown that the change in elasticity occurring when an iron wire is magnetized will modify the relation between the intensity of magnetization and the elongation, and it has been assumed that, except for heavily loaded wires, this effect will be very small. Bock[*] found as a result of his experiments that magnetizing soft iron made it more incompressible, and that the change in elasticity was less than one half per cent. He could not find any relation between the intensity of magnetization and change in elasticity, so that it is impossible to give more than a probable maximum to the correction it is necessary to make in the curves given in this investigation.

If we take $B = 20,000$,

$$\frac{B^2}{8\pi} = \frac{1}{2\pi} \times 10^8 \text{ dynes per square centimetre,}$$

and

$$\frac{\delta l}{l} \times 10^7 = -\frac{\frac{1}{2\pi} \times 10^8}{M} = -73.$$

A change of $\frac{1}{2}$ per cent. in $\frac{\delta l}{l}$ would give a correction of $\cdot 005 \times 73 = \cdot 4$ of a unit. This correction may therefore be neglected, as errors greater than this would occur in measuring B.

It was also assumed that when the wire was not stretched except by the jacket, the correction might be neglected.

The weight of this was 350 grams or 42,000 dynes per square centimetre, then

$$\frac{\delta l}{l} \times 10^7 = \frac{42000}{M} \times 10^7 = 200.$$

A change of $\frac{1}{2}$ per cent. in 200 is $1 \cdot 0$. Consequently the curves marked no load are not significantly changed by making this correction.

But when we consider the case of the wire loaded with 750 kilograms per square centimetre, we get, by similar calculation, a correction of 15 units ; and for the wire under the greatest tension, 1750 kilograms per square centimetre, a correction of 40 units. Since the magnetism makes the metal more incompressible, this correction enters as a contraction

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[*] Bock, *loc. cit.*

and must be added to the ordinates of the curves plotted on fig. 5. It is impossible to say how these curves would be affected by the correction, but probably the correction increases with the intensity of magnetization.

Changes in the length of the wire due to variations in temperature are another possible source of error. These changes take place more slowly than the elongation produced by the magnetization, so that the two effects may be separated. To retard them still more the core of the solenoid was made of two co-axal cylinders and the space between them filled with water. With this arrangement the current could be applied, the reading taken, and the current shut off before the gradual change of the zero point due to the heating of the wire by the current could be observed. Changes in the temperature of the room when they did occur were too slow to noticeably affect the results.

Summary.

The following is a summary of the results obtained by this investigation :—

1. A relation has been obtained between the elongation due to magnetization and the intensity of magnetization of soft iron. When the elongation has been corrected for the contraction caused by the $B^2/8\pi$ force, the relation may be expressed thus :—A rod of iron elongates slowly until an intensity of about 800 is reached. After that point the rod elongates more rapidly and attains a maximum value of about 60×10^{-7} part of its length at an intensity of 1200. With greater intensities the elongation diminishes, the curve being approximately a nearly vertical straight line.

2. Hardening the wire diminishes the corrected elongation, and the wire attains its maximum length in a less intense field.

3. It has been shown that when the wire is stretched, the change in elasticity due to the magnetization produces an important effect. Neglecting this correction, the effects of stretching are similar to those caused by hardening the wire.

XXX. *Of the Kinetic Theory of Gas, regarded as illustrating Nature.* By GEORGE JOHNSTONE STONEY, *M.A., D.Sc., F.R.S., Vice-President, Royal Dublin Society* *.

SCIENCE may be defined as the investigation of how nature works, of how and why events in nature occur.

This investigation is best carried on by employing the Physical Hypothesis, viz., that the objects of nature act on one another, either directly (action at a distance), or through intervening media (which by many is supposed to be an essentially different kind of action). Now, the objects of nature, in the more strict sense of that phrase, are syntheta of human perceptions and ultra-perceptions ; and syntheta of perceptions cannot be what really act. Nevertheless, it is eminently useful to carry on our investigation under the physical hypothesis that it is they which act, and to confine our efforts to tracing out what effects this action must be supposed capable of producing, and under what laws it must operate, in order that it may account for what occurs in nature. This, however, is felt by many persons to be too abstract an attitude of mind ; and to satisfy them, and create the plausibility which they demand, by relieving the fundamental conceptions of what is oppressively felt as the absurdity of supposing that syntheta of perceptions act, it is usual to supplement these syntheta by piling an aërial Pelion upon this solid Ossa, and by supposing that in addition to the *sensible object* which occupies any portion of space there is what is called *its material substance* occupying the same position, which, partly directly and partly by its motions, acts on other material substances [the æther being one of these material substances]. According to this, which is the prevalent hypothesis among both scientific and non-scientific men, it is these substances which travel about through space ; and the sensible objects, which are what we see and feel, are supposed to accompany them in their wanderings by reason of the way in which they, the substances, act (usually through intermediate material agencies) upon our organs of sense †.

This is the usual point of view: but more careful thinkers

* From the Scientific Proceedings of the Royal Dublin Society of the 26th of June, 1895. Communicated by the Author.

† The author has endeavoured to trace out what it is that really occurs in all such cases. See his paper "On the Relation between Natural Science and Ontology," in the Scientific Proceedings of the Royal Dublin Society, vol. vi. (1890) p. 475.

will do well * to eschew this somewhat convenient, but by no means necessary, encumbrance upon the unadulterated process of physical investigation which treats the sensible objects themselves, the bare syntheta of perceptions and ultra-perceptions, as though they were what brought about the changes that occur in nature ; and which exclusively occupies itself in tracing out the laws that must, under this hypothesis, be in operation in order that the effects may be what they are.

Another and a very useful scaffolding which helps us in building up our investigation, is the introduction of forces between the physical cause (which is always the vicinity of some natural object) and the effect to be attributed to it under the physical hypothesis.   We are thus enabled to speak of the acceleration of a stone in its fall towards the earth either as being due to the neigbourhood of the earth, or as being caused by a force of gravitation which acts on it, which force is, in its turn, regarded as brought into existence by the proximity of the earth to the stone.   The introduction of this piece of intermediate scaffolding is of great service—

1. Because the force can be represented by a line whose length accurately represents the intensity, and whose direction accurately represents the direction of the effect upon the stone of the vicinity of the earth ;

2. Because the same effect upon the stone might have been due to other physical causes, as, for example, to a spring urging it forward, in which case the same piece of scaffolding, a force represented by the same line in the same position, would occupy its place between the cause and the effect ; and

3. Because the effect might have been different, while the physical cause remained the same—thus, if the stone lay on the ground, what the vicinity of the earth would have occasioned is stress between the stone and the ground.

Accordingly by referring effects in nature to the operation of forces, we are enabled in each case to indicate with accuracy the intensity and direction of the effect, without having to specify (*a*) which of several possible physical causes is the one in operation, or (*b*) which of the possible kinds of effect is that which is being produced : and this in practice is found to be an immense convenience.

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* This course is much to be preferred, because it effectually avoids the risk of throwing dust in our own eyes.   The justification of the Physical Hypothesis is its utility, not its truth—its incomparable efficiency as a means of investigating nature ; and it is better, though not essential, that students of Physics should make no mistake about a matter of this kind.

Such is an outline of the principles that underlie the dynamical investigation of nature, which is the form of investigation that penetrates most deeply into its secrets.

The dynamical investigation of nature being the most complete from the physicist's standpoint, is of course to be preferred to any other wherever it can be employed. Our present knowledge of astronomy, of rigid dynamics, of elasticity, of hydrodynamics, are among its great achievements. But there are other sciences in which we cannot penetrate so close to the origin of things, but which are, nevertheless, amenable to mathematical treatment onwards from a station less deep-seated. In these we begin with happily chosen equations, the truth of which we have not succeeded in tracing to their dynamical source in nature, but the consequences of which we can calculate and compare with what we observe to occur. Of this kind are the exquisite theory of light which was developed by M'Cullagh, and the enormous strides which our knowledge of electricity has made within the last half century, culminating in the marvellous electromagnetic theory of light.

In all such sciences we are greatly helped by mechanical illustrations, which may be regarded as working models, that, though they do not in the least profess to represent the unknown dynamical condition which exists in nature, furnish us with an apparatus which operates in ways that we can both compute and conceive, and which produces results that, in some important respects and within ascertainable limits, follow laws the same as or analogous to those that prevail in the part of nature which is illustrated by them. Of this kind is that most useful and simplest wave-theory of light which represents it by an undulation of mere transverse vibrations. Of the same kind are the various attempts to represent the " texture," which must prevail in the luminiferous æther [*]. And somewhat akin to these are those instructive analogies which can be traced out between different sciences, wherever in both the same differential equation governs the progress of events. Thus, when a current of electricity is turned on to a circuit, the current penetrates the wire from its surface towards its core, by the same law as that by which heat would, by conduction, be carried inwards from the surrounding dielectric—a process already familar to us, and which, therefore, makes the sequence of events in the other case easily conceived.

Again it must be remembered that in every dynamical

[*] See Scientific Proceedings of the Roy. Dubl. Soc. vol. vi. p. 392, or Philosophical Magazine for June 1890, p. 467.

investigation, what the mathematician really investigates is not the problem presented by nature, but some simplification of it. The legitimacy of this process and its value depend upon the important circumstance that, in dynamics, a slight change in the data leads only, at least for a time, to a slight change in the result. Thus in computing the mutual perturbations of the planets, the planets may be treated as though they were spheres, made up of untextured spherical shells each of a uniform density throughout; and it may be left out of account that they approach to being spheroids, with mountains on their surface, irregularities of a like kind at greater depths, rocks in those mountains, minerals in those rocks, a different molecular texture in each mineral, tidal strains, heat expansions by day, contractions by night, and so on—perhaps seas and an atmosphere, vegetation and animals, all in constant and complicated movement; with numberless other details. Now it is legitimate to omit all these from our calculation, for though every one of them produces its effect in actual nature, the difference between the outcome of their joint operation and that computed from the greatly simplified data of the mathematician is too small to make any approach to being perceived by any human agency. Hence, for any purpose which is of use to man, the approximation arrived at by the simpler problem is sufficient, wherever the errors are of such a nature that they are not cumulative. Nevertheless, it should be clearly recognized that it is a mechanism illustrating nature, and not nature itself, that has been mathematically investigated. So it is with all dynamical investigations: the data of nature have to be simplified to bring the task within the range of man's power over mathematical analysis; and the result is satisfactory because of the important fundamental principle referred to above, that in dynamics a slight modification of the data furnished by nature may be safely made, because it leads only to there being a small difference between the calculated result and that which occurs in nature —of course care being taken in each case that the approximation of the computed result to what occurs in nature shall be sufficiently close for the object we have in view.

These criticisms need to be pressed with special emphasis when we are examining investigations into the dynamical condition of gases. Here we have to substitute for the data of nature others which differ from them in undesirable ways and to an undesirable extent, in order to arrive at data simple enough to be available as a basis for mathematical deductions. Nevertheless, some of the results are not appreciably affected by this too great simplification of the data: for instance,

those which are consequences of such general facts as that the molecules spend most of their time in travelling about in straight lines like missiles, without a preponderance of the kinetic energy of the motions in any one direction ; and the further fact that the interchange of energy which occurs during the encounters, and the immense number of these encounters, lead to a rapid distribution to other motions of any excess of energy which any one motion of any one molecule may possess, and thus both equalize the pressure throughout the gas and establish the prevalence of a constant average ratio between that portion of the energy which manifests itself in the journeyings of the molecules, and that which is occupied in internal motions of the Ba class.

In order to make this language intelligible, it is necessary to explain that in treating of gases it is convenient to use the word *motions* in a generalized sense, so as to include both motions proper and all other events which are brought about by imparting energy to the gas, and which thereby become depositories of energy. These motions or events may be first divided into the two classes A and B, external and internal events. The A or external events are simply the motions of the centres of inertia of the molecules between their encounters ; the B events are rotations or other motions, or changes of configuration, of the parts of a molecule relatively to one another, or electrical or other events ; any events, in fact, which can be brought about by an expenditure of energy. These may all be spoken of either as motions or events, using the term motions in its generalized sense.

Again, the B events require to be subdivided into three classes : Ba events, which readily exchange energy with the A events, *i. e.*, which are affected by the speed with which two molecules plunge into one another when an encounter takes place, and which in turn contribute in a marked degree towards determining with what velocities they shall separate when the encounter is over. In contrast to these, the Bc events (if any such exist, as is perhaps probable if the vortex theory of matter is true) are such as are *completely* isolated from the A and Ba events, and therefore neither gain nor lose energy in the encounters. Between the Ba and Bc events stand Bb events, which seem to be a conspicuous part of what is actually going on in all the real gases of nature. These Bb events are not wholly unaffected by the encounters, but in any one encounter gain or lose but little energy ; while after millions of encounters, the transference of energy, perhaps chiefly in one direction—from them to other events— may be appreciable. Events of this kind may produce even

conspicuous effects in times which appear to us very short, since in the ordinary air about us each molecule meets with a million of encounters in something like the seventh part of the thousandth of one second of time. In attempting to interpret the results furnished by our dynamical investigations, the extraordinary * rapidity with which the molecular events succeed one another in the actual gases of nature must be fully allowed for.

Another matter to be kept carefully in mind is that most of the dynamical investigations go on the assumption that interaction between molecules, and the interaction within a molecule of one part of the molecule upon another *are the only forces that intervene* ; whereas in all actual gases there is also a continuous interchange of energy going on between some of the internal events of the molecules and the ocean of unceasing ætherial undulations in which they are immersed.

One most remarkable and instructive dynamical theorem is due to the keen insight of Clerk Maxwell and of Professor Boltzmann.

Maxwell discovered the important theorem that if generalized coordinates be used to represent the motion of any system of bodies, and if the *vis viva* can be expressed as a sum of squares of momenta † of these coordinates, then the average energy will, if once equally divided among the terms of this series, continue to be so divided.

Boltzmann has extended this theorem into the following:—

If the *vis viva* can be expressed as a symmetrical function of the second order of the momenta (which may include both squares and products) then momentoids—linear functions of the momenta—can be so constructed that the *vis viva* shall be a sum of squares of these momentoids multiplied by functions of the coordinates ; and the average energy, if at any time equally divided, will thenceforth continue to be equally divided between the terms of this expression.

Under the Maxwell Theorem it is between the momenta, under the Boltzmann-Maxwell Theorem it is between the momentoids, that the equal partition of energy takes place. The number of the momentoids is the same as of the momenta, and each of these latter is associated with a distinct degree of freedom in the system. Hence, when the Maxwell Theorem holds, the energy is equally divided among the degrees of

* See the description of an illustrative model in the last paragraph of this paper.

† A momentum may be defined as the differential coefficient of one of the coordinates with respect to time, multiplied by a coefficient which may be any function of the coordinates.

freedom ; but it is between certain quasi-groups of these degrees of freedom that the partition takes place under the Boltzmann-Maxwell Theorem. These quasi-groups, like the momentoids which define them, are of the same number as the degrees of freedom.

In most cases, where the only forces intervening are inter-actions between parts of the system, the energy can be ex-pressed in the form required by the theorem. But this is not the case when certain external forces * come into opera-tion, as, for example, when the æther acts on molecules as well as the molecules or parts of a molecule on one another.

Nevertheless, the theorem is of value in the interpretation of nature, because in many cases the æther intervenes some-what as perturbating forces do in the case of the planets, modifying but not annulling the dynamical condition which would prevail if the sun's attraction alone exercised dominion over them.

On the other hand, it must be remembered that such a vast number of molecular events are crowded together within a duration that appears very short to us, that small effects have superabundant opportunity of gradually accumulating and becoming conspicuous, within a small fraction (*e. g.* within the thousandth part) of one second of time.

In estimating the average energy, the average may be struck either over a great succession of events happening to one molecule, or over what occurs simultaneously to a vast number of molecules †.

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* Certain internal forces also : for example, such as manifest themselves in a change of state or in a chemical reaction. The theorem does not hold over intervals of time extending from an epoch before to an epoch after catastrophes of this kind.

† In Maxwell's and Boltzmann's investigations the averages have been struck only in the second way, viz., over what occurs simultaneously to a vast number of molecules ; but general dynamical considerations seem to warrant our feeling sure that the average, if struck in the other way, *i. e.*, over a great succession of events happening to one molecule, would have the same value—on the understanding, of course, that the molecules are alike, and that the condition of the gas, in the respects with which the theorem is concerned, is a persistent condition.

In fact, it then seems safe to assume that in the course of a sufficiently long experience the coordinates and momenta of any one molecule will have approximately assumed all the combinations of values that the coordinates and momenta of any other molecule shall have had.

This is the same kind of assumption as the familiar assumption that if *n* dice (*n* being a sufficiently large number) were thrown simultaneously, sixes would turn up on a number of these dice which bears to the number of times sixes would turn up on one die thrown *n* times, a ratio which may be treated as a ratio of equality.

The importance and value of these results depend :—

1. On the small volume and the short time, as estimated by what are involved in human experiments, which suffice for the requisite averages—since each cube of a micron (the thousandth part of a millimetre) in the volume of the gas contains about 1000 millions of molecules * if it be under the same pressure and temperature as atmospheric air, and each of these molecules meets with about seven million encounters within the thousandth part of one second.

2. They also depend on the principle recited above, viz.— that if the data of a dynamical theorem be slightly altered, the conclusions are only disturbed to a small extent.

3. And they depend on the circumstance that the forces to be taken account of in applying the theorem may be confined to such forces as are concerned in those events which either directly or indirectly influence the motions of molecules in their journeys between their encounters. If, accordingly, there be any events of the kind which we have termed B*c* events, they and the forces concerned in them may be kept outside the theorem, and may exist and involve any amount of energy ; which energy is, however, additional to that which in the theorem is regarded as the total energy, which is to be understood as the total of the energy of the events with which the theorem is concerned.

The following mechanical illustration, which is that usually employed, will enable us better to grasp the meaning and appreciate the value of these remarks. In it I will suppose the gas to be of one kind, with molecules that are all alike, and that the number of molecules and the average duration of a journey are what they are in atmospheric air at the surface of the earth.

The simplest way of fulfilling the condition that the expression for the energy shall be a sum of squares, is to provide a mechanical model in which the whole energy is kinetic; and the simplest way of securing this is to suppose each molecule to be a rigid elastic body, with a frictionless surface. The expression for the energy of the molecule will then take the familiar form :

$$T = \tfrac{1}{2}\left[M(u^2 + v^2 + w^2) + A\omega_1^2 + B\omega_2^2 + C\omega_3^2 \right],$$

where the letters have their usual meanings. Here each term in the expression corresponds to one of the six degrees of freedom of the rigid body, and the theorem states that the

* See Phil. Mag. for August 1868, p. 141.

time-integrals of the several terms of this expression are equal, and that the average value of T is 1/Nth of the total energy in the gas, N being the number of molecules ; in other words, that the molecule exhibits one-sixth of its share of the total energy in each of the following ways, viz. :—1°, in its journeyings east and west ; 2°, north and south ; 3°, up and down ; 4°, 5°, 6°, in spinning on each of its three principal axes. To simplify the conception as much as possible, we may suppose our model of a molecule to be a smooth ellipsoid of uniform density.

Let us next represent the molecules by ellipsoids of revolution. The full expression for the energy of such a body is—

$$T = \tfrac{1}{2}[M(u^2 + v^2 + w^2) + A\omega_1^2 + B(\omega_2^2 + \omega_3^2)], \quad . \quad (1)$$

but for the purposes of the theorem it may * be reduced to—

$$T' = \tfrac{1}{2}[M(u^2 + v^2 + w^2) + B(\omega_2^2 + \omega_3^2)], . \quad . \quad . \quad (2)$$

since rotation round the axis of symmetry can neither be set going by the kinetic energy with which the molecules collide, nor if maintained in any other way can it in the least influence the values of u, v, and w.

The model when dealt with in this way is instructive, because it illustrates, as Mr. Bryan has pointed out (Proceedings of Cambridge Phil. Soc. of Nov. 26, 1894), how a motion may exist in a molecule which does not come under the theorem, and which therefore may be going on with any amount of energy.

To describe the situation in other and very convenient language, the motions of translation of the ellipsoids of revolution between their encounters are A events, and the energy of these events, viz. :—

Average value of $\Sigma\tfrac{1}{2}M(u^2 + v^2 + w^2)$

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* It is very necessary to bear in mind that, so far as the theorem is concerned, it is optional with us whether we make this reduction from 6 to 5 terms or not. But if we retain the term $\tfrac{1}{2}A\omega_1^2$, we must remember that the theorem only deals with motion subsequent to an initial condition *in which an equal partition of energy had been made* among the terms. It states that *if* this condition existed initially, it will continue subsequently ; and this is evident so far as the rotation round the axis of symmetry is concerned, since, if this rotation were once set up, it would continue unchanged. For some purposes we must retain the six terms, *e. g.* in order to see how the transition from the case of a solid of revolution to the case of a solid which differs but little from a solid of revolution, takes place without an abrupt change in the effect predicted by the theorem, so as to comply with the general principle of continuity in dynamics.

is 3/5 of the whole of that energy of the mechanical model which comes under the notice of the theorem. The rotations ω_2 and ω_3 are Ba events, and their energy, viz. :—

<p align="center">Average value of $\Sigma \frac{1}{2} B(\omega_2{}^2 + \omega_3{}^2)$</p>

is 2/5 of the energy dealt with by the theorem. The rotation ω_1 is a Bc event, which can be kept outside the theorem. In it, accordingly, any amount of energy may reside.

Another instructive mechanical illustration is constructed by considering each molecule as a rigid ellipsoid of one uniform density surrounded by a rigid envelope of another uniform density, extending from the surface of the ellipsoid to the smooth surface of an outer concentric sphere (see Bryan, *loc. cit.*). Such a complex molecule may represent a diatomic molecule with only three of its degrees of freedom operated upon during collisions. Here the energy of the molecule is

$$T = \tfrac{1}{2}\left[M(u^2 + v^2 + w^2) + A\omega_1{}^2 + B\omega_2{}^2 + C\omega_3{}^2 \right],$$

whereas the part concerned in the theorem is only

$$T' = \tfrac{1}{2} M(u^2 + v^2 + w^2),$$

since the external surface being a smooth rigid sphere round the centre of inertia, the collisions cannot set up rotations.

In this case u, v, and w are A events ; and, on the average, divide equally among themselves the share of energy coming to this molecule under the theorem. At the same time the rotations ω_1, ω_2, ω_3 are Bc events, and may be going forward, subject only to the equations of the rotation of a rigid body round its centre of inertia, viz. :—

$$T'' = \tfrac{1}{2}(A\omega_1{}^2 + B\omega_2{}^2 + C\omega_3{}^2),$$

$$G = A^2\omega_1{}^2 + B^2\omega_2{}^2 + C^2\omega_3{}^2.$$

Their energy T'' may, accordingly, be of any amount in each molecule separately.

We have hitherto had only A, Ba, and Bc motions in our illustrative models. Bc events are of little practical interest ; whereas the study of Bb events is of much use, since they are probably present in large amount in actual gases. It is easy to modify our mechanical illustration so as to introduce events of this class. It may be done in either of the models we have employed by imagining the surface to be roughened (either by a small amount of friction or in the sense of being covered with slight frictionless elevations and depressions), and by

<p align="center">2 C 2</p>

supposing electrons (the charges of electricity which are associated with chemical bonds, and which, so long as they are undisguised, are acted on by the disturbance perpetually going on in the surrounding æther) to be carried about by the internal or B events of the molecule. To complete the picture we may suppose most of these electrons to be so connected with the internal economy of the molecule that they can only perform evolutions that are resolvable into partials that have definite periods.

Before this change the internal events were B*a* and B*c* events, but, owing to the introduction of the slight roughness, the B*c* events have become B*b* events; *i. e.* they have acquired the power of very slowly, and through a great number of collisions, affecting *u*, *v*, and *w*, which are the A events. But even if the roughness be so slight that they require a million of collisions to impart a sensible proportion of their energy to the A events, they will accomplish a protracted task of this kind in about the seventh part of the thousandth of one second, if, as we have supposed, the rapidity of events in our model is as great as it is in gases at atmospheric pressures and temperatures. Now, observations with the phosphoroscope indicate that the persistence of B*b* events, when once excited, is in all the observed cases much greater; so that the outer surfaces of our model molecules should be *very* nearly, though not quite, smooth. Other experiments which are in progress seem to show that, in some instances at least, the energy radiated away from phosphorescent events is much less than that which they lose by conduction, *i. e.* by imparting energy to A or B*a* events. Now an excessively small defect in smoothness, such as we have supposed, would not prevent the Boltzmann-Maxwell distribution of energy from being nearly the actual distribution among A and B*a* events, wherever the other conditions of the theorem are, or are nearly, fulfilled; while side by side with them any amount of energy may be maintained in B*b* events by the electromagnetic waves which unremittingly traverse the surrounding æther, or may be set up by chemical reaction*.

* It is easy to contrive other useful models, and to treat them like those in the text. Of this kind are models with spherical, spheroidal, or ellipsoidal outer surfaces, but with centres of inertia, either displaced from the centre of figure, or moving about it under definable conditions; or with more than one body inside the outer surface, and either concentric or not concentric with it, and with viscous or other connexions which would provide for various kinds of interaction; or with the rigid outer surface discarded, and central forces put in its place—a substitution which either need not, or need not more than a little, alter the condition that the average energy shall be a sum of squares; and many others. Each

Another important matter to be referred to is that in the cases in which the theorem holds good, γ, the ratio of the two specific heats (at constant pressure and at constant volume) has the following value—

$$\gamma = 1 + \frac{2}{m},$$

where m is the number of terms—each the square of a momentoid multiplied by a selected coefficient—in the expression for the energy. Now observation gives γ in many cases, and we thus arrive, by the foregoing equation, at m, the number of the terms in the expression of T, which is the same as the number of degrees of freedom in the molecule of those events with which the theorem is concerned, if the constitution of the gas be such that the theorem approximately applies to it. To what motions these degrees of freedom are to be supposed to correspond will depend on what experiment has been made use of in determining γ. If the experiment is one that lasts a long time—for instance a whole second or more—then the Bb motions as well as the A and the Ba motions will usually have had abundant time to operate ; but if it depends on rapidly changing events, as where the velocity of sound in the gas is the fact that is ascertained, then we may expect that some of the Bb events will be unable to influence the result. It is very convenient to distinguish the internal events into Ba motions and Bb motions ; but it must be remembered that this distinction is one of degree, and that, although in most gases they appear as different as is the chin from the cheek, it would nevertheless be quite as impossible to indicate precisely where the one ends and the other begins.

The following table of the best determinations of γ is given by Mr. Capstick in ' Science Progress ' for June 1895. I have added the last two columns in which are given the values of m which the determinations would suggest, if the Boltzmann-Maxwell theorem could be regarded as holding good for the gas.

In this table, γ is the ratio of the two Specific Heats, as given by observation ; m is the number of degrees of freedom of each molecule ; and $m-3$ is the number of degrees of freedom of its B, or internal, motions : according to the Boltzmann-Maxwell theorem.

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may be in its way instructive if we use it to enable us to picture modes of action that occur in gases, and if we are careful not to be misled into fancying that any of our models can be accepted as even in a remote degree resembling the state of things that does prevail within the molecules of matter.

Name of Gas.	Chemical Formula of Molecule.	Atomicity of Molecule.	Observed Value of γ.	Computed Value of	
				m.	$m-3$.
Mercury	Hg	1	1·67	3·0	0·0
Argon	Not yet known.		1·65	3·1	0·1
Transparent Gases. { Hydrogen............	H$_2$		1·41	4·9	1·9
Nitrogen	N$_2$		1·41	4·9	1·9
Carbon monoxide ..	CO		1·40	5·0	2·0
Hydrochloric acid ..	HCl		1·39	5·1	2·1
Hydrobromic acid ..	HBr		1·42	4·8	1·8
Hydriodic acid ...	HI	2	1·40	5·0	2·0
Coloured Gases. { Chlorine	Cl$_2$		1·32	6·2	3·2
Bromine	Br$_2$		1·29	6·9	3·9
Iodine	I$_2$		1·29	6·9	3·9
Iodine chloride ...	ICl		1·31	6·5	3·5
Carbon dioxide...............	CO$_2$		1·308	6·5	3·5
Nitrous oxide	N$_2$O	3	1·310	6·5	3·5
Sulphuretted hydrogen ...	SH$_2$		1·340	5·9	2·9
Carbon bisulphide	CS$_2$		1·239	8·4	5·4
Ammonia	NH$_3$	4	1·30	6·7	3·7
Methane	CH$_4$		1·313	6·4	3·4
Methyl chloride	CH$_3$Cl		1·279	7·2	4·2
Methyl bromide	CH$_3$Br		1·274	7·3	4·3
Methyl iodide	CH$_3$I		1·286	7·0	4·0
Methylene chloride	CH$_2$Cl$_2$	5	1·219	9·2	6·2
Chloroform	CHCl$_3$		1·154	13·0	10·0
Carbon tetrachloride	CCl$_4$		1·130	15·4	12·4
Silicon tetrachloride	SiCl$_4$		1·129	15·6	12·6
Ethylene	C$_2$H$_4$	6	1·260	7·7	4·7
Vinyl bromide	C$_2$H$_3$Br		1·198	10·1	7·1
Ethane	C$_2$H$_6$		1·180	11·1	8·1
Ethyl chloride	C$_2$H$_5$Cl		1·187	10·7	7·7
Ethyl bromide	C$_2$H$_5$Br	8	1·188	10·6	7·6
Ethylene chloride...........	C$_2$H$_4$Cl$_2$		1·137	14·7	11·7
Ethylidene chloride	C$_2$H$_4$Cl$_2$		1·134	14·9	11·9
Allyl chloride	C$_3$H$_5$Cl		1·137	14·7	11·7
Allyl bromide	C$_3$H$_5$Br	9	1·145	13·9	10·9
Alcohol	C$_2$H$_5$OH		1·133	15·1	12·1
Propane	C$_3$H$_8$		1·130	15·4	12·4
Normal propyl chloride ...	C$_3$H$_7$Cl		1·126	15·9	12·9
Isopropyl chloride	C$_3$H$_7$Cl		1·127	15·9	12·9
Isopropyl bromide	C$_3$H$_7$Br	11	1·131	15·4	12·4
Ethyl formate	HCO·OC$_2$H$_5$		1·124	16·1	13·1
Methyl acetate	CH$_3$CO·OCH$_3$		1·137	14·7	11·7

Postponing for the present the observations which the details of this table suggest, and taking a general survey of it, it was difficult to see how the small number of degrees of freedom suggested by the ·Boltzmann-Maxwell Theorem, as shown in the last column of this table, could be reconciled with the known great complexity of the molecules of which real gases consist, until Professor FitzGerald pointed out (Proceedings of the Royal Society for February 14, 1895, p. 312) that the æther, acting on the electrons, which in turn are intimately connected with the ponderable matter of the molecule, must perform the function of a more or less perfect linkage between molecules, compelling them, so far as some of their motions are concerned, to move together in swarms. This follows at once from the circumstance that the electro-magnetic waves, in which radiant heat and light consist, are hundreds of times longer than the average intervals between molecules in gases at the pressures and temperatures at which the gases in the table were when experimented on to deter-mine the value of γ.

There may be a hundred degrees of freedom in a molecule. Of these the three which are concerned in its power of travelling about between its encounters are not affected by what goes on in the æther, and are therefore inalienably associated with that molecule ; but as regards the 97 others, the linkage through the æther may be such that millions of molecules are, as it were, held in one grasp, either firmly or more or less loosely. Accordingly, as regards any one mole-cule, these 97 may make no appreciable increase, or may make but a moderate increase to the three which in all cases must attach to the molecule. These three are A events, and along with them we should class the few Ba events which have no electrons associated with them, of which there seem to be two in several of the transparent diatomic gases.

We here seem to be led to another conclusion. If the æther were a mere linkage, and not at the same time an agency which excites simultaneous motions within swarms of molecules, it would appear from the Boltzmann-Maxwell theorem that none such would in any appreciable degree be brought into existence by the encounters between molecules. If, for example, the expression for T contains two B terms in-stead of 97, then only $\frac{2}{5}$ of the energy which is taken account of in the theorem would be available for distribution among 97 distinct kinds of motion, and therefore too little for any but a very few of them to be able to exhibit an observable effect. The rest, the Bb events, would all depend for their activity upon energy reaching the molecules as radiant heat

or in some other form through the æther, or in some other way, as, for example, from a disruption of chemical bonds. But though the encounters would be unequal to the task of arousing them from a state of quiescence, they, on their side, if brought into a state of activity by some other agency may be able to impart energy to A and Ba events, which are the proximate dynamical cause of the ordinary gaseous laws. This peculiar behaviour, whereby energy passes more freely one way than in the opposite direction, is a dynamical consequence of the linkage between molecules to which Professor FitzGerald has called attention. Owing to this linkage the encounters may have to produce an effect on a platoon of molecules in order to affect the Bb motions of any one of them ; and as these encounters are many and irregular their aggregate effect can be but small wherever the linkage is effective ; while, as regards the reaction, the body of linked Bb motions act in each encounter on the A or Ba motions of a single molecule and may produce a considerable effect on them. The dynamical relation is analogous to what would prevail between a number of light pellets bombarding a massive body on all sides. Their effect on the motion of the massive body is small, while its effect on their motions is large. It seems to be in this way that radiant heat can warm a gas through the lines in its spectrum, very slowly in the more transparent gases, less slowly in coloured gases.

An electron within a molecule may be associated with either its Ba or its Bb motions. Thus, when a phosphorescent body has been exposed to suitable light, it is an electron associated with Bb motions that is primarily acted on by the æther. Now phosphorescence is a very prevalent property of bodies, inasmuch as it has been ascertained by the phosphoroscope that a large proportion of the substances about us are phosphorescent. And although most of them, after being stimulated, retain their power of radiating light for but the fraction of a second, there are some phosphorescent substances in which it lasts for hours. It must be remembered that any fraction of a second which the phosphoroscope can detect is an immense duration as regards the rapidity of molecular events. Accordingly it is with Bb events that we are here dealing. All Bb events are sluggish from the molecular standpoint in handing over any excess of energy they may possess, either directly or indirectly, to the motions of translation of the molecule. But viewing the matter from our human standpoint, it is convenient to distinguish those which can accomplish this in a small fraction of a second from those which take so much longer a time that we can

easily perceive it. We may call the first Bb_1 events. These are they which can effect the transfer through some few millions of encounters. And we may call the still more isolated events Bb_2 events. These latter, for example, manifest their existence when phosphorescence lasts for a whole second or more—truly enormous durations as regards molecular activities.

When an electron is associated with Ba events it will promptly transfer over any excess of energy it receives from the æther to u, v, and w, the translational velocities of the molecule. Accordingly, on the one hand, the temperature and pressure of the gas will increase, on the other the ætherial undulations that acted on the electron will have ceased—in other words, the gas is one that has an absorption-spectrum.

If, at the other extreme, the electron is associated with Bc, or absolutely isolated events, a beam of light passing through the gas will, if it contain certain rays, set these electrons moving. They, however, will not impart any of their acquired energy to other events going on in the gas, but will continue swinging in all the molecules in coincidence with the electromagnetic wave as it sweeps past them in the æther; thus restoring to the latter the same amount of energy which they received, and in the form of an undulation travelling at the same rate, and in the same direction, and oscillating in the same periodic time. Thus, so far as regards the motion of this electron, the gas is transparent.

Between these extremes electrons associated with Bb events will lie, and may produce any intermediate event.

It is very instructive to glance over the determinations of γ in the table on p. 374. Take, for example, the diatomic gases. Six of them are transparent, and the other four are coloured. The transparent gases furnish values for γ which all lie in the neighbourhood of 1·4, which is the value which would correspond to a molecule having five degrees of freedom if the conditions of Boltzmann's theorem were completely fulfilled. In transparent gases they are probably not much interfered with, since in them the electrons are associated with Bb_2 events, and it is only after *many* millions of encounters that the æther can, through them, sensibly affect the A and Ba events with which the theorem is concerned. On the other hand, in the coloured gases one or more electrons (in these special gases probably something like six or eight electrons, judging from their spectra) are associated with Bb_1 events, and largely affect the events with which the theorem is concerned. They accordingly cause γ to be different from what it would be if the dynamical interactions stood alone,

which, judging from the transparent gases, we may conclude would be 1·4, furnished by 5 degrees of freedom. The B*b* motions in question would probably add something like three times 6 or 8 more degrees of freedom if the molecule stood alone, but by reason of the linkage only some fraction of this addition has to be made. It appears from the table that in chlorine, which is the least deeply-coloured gas, that is, the gas in which the linkage is most effective, the addition to be made is of 1·2 degrees of freedom; while in bromine and iodine an addition of 1·9 degrees of freedom has to be made, indicating that the linkage is more lax in these gases.

Since in so many bodies the electrons seem to be associated with events which are very much isolated from those that are chiefly affected by the encounters, the modification of the dynamical condition which is introduced through them may be regarded as a perturbation. It would perhaps not be impracticable to discover in what way perturbating forces, not obeying the conditions of the Boltzmann-Maxwell theorem, can influence the results of that theorem. This would be of much value; and if it can be made out, will perhaps explain why in some transparent diatomic gases the value of γ is above 1·4, while it is less than that value in others. The reason probably is that in hydrogen, nitrogen, and hydrobromic acid the motions associated with their two B*a* degrees of freedom are able to rouse a certain amount of activity in adjoining B*b* events, and that thus a part of their energy gets to be exposed to linkage.

Hitherto we have regarded molecules as acted on in two ways only—by dynamical interactions between or within the molecules, and by the effect of electromagnetic waves on such of the electrons as are undisguised charges of electricity. But there are other ways in which molecules may be acted on, of which the most conspicuous intervenes energetically on those critical occasions when chemical reaction takes place. Here it is the electrons that are primarily concerned, as is manifest from Faraday's law of electrolysis. In cases of friction also, or of disruption of a crystal, it is manifest that some of the electrons are started into activity. In fact it may be presumed that the intermolecular bonds within a crystal are fundamentally of the same kind as the interatomic bonds within a molecule, and that in both it is interaction between electrons that is principally called into play. It should also be noted that the number of electrons within an atom may be greater than its place in Mendeléeff's table would seem to suggest, as is, for example, evidenced by the chemical behaviour of potassium.

In chemical reactions, if the product is gaseous, and if the electrons which are set swinging are associated with Ba events, the most obvious effect is a sudden increase of temperature and pressure ; if associated with Bb_2 events the most obvious effect is a flash of light ; and if associated with Bb_1 events both effects will be conspicuous : and this, in accordance with what we learn through the phosphoroscope, would seem to be what most frequently happens.

It seems probable that it is when excited by chemical reactions that electrons produce their most conspicuous luminous effects, whether in flames or in so-called incandescent spectra. It should be remembered that as electrons are for the most part associated with Bb motions within the molecule, it may happen that they but slowly influence the temperature of the gas as indicated by the thermometer, and that accordingly the luminous effects may be greatly in excess of what a mere incandescent body at the same moderate temperature could produce. Hence the phrase incandescent spectrum is not always appropriate, since the supposition that the temperature inside a Plücker tube must be high is erroneous.

These inferences are entirely borne out by the recently published observations of Professor Lewes upon gas-flames (see Proceedings of the Royal Society for March 7 and March 21, 1895). He finds that the first group of chemical changes which the issuing gas undergoes are brought about by *radiant* heat ; in other words, by electromagnetic waves in the æther acting on those electrons which are concerned in the chemical changes, and which, from their not being affected by convected heat, must be associated with Bb, and not with Ba events. In this way

$$\text{H} \cdot \text{C} : \text{C} \cdot \text{H} \qquad \begin{matrix} \text{H} \cdot & & \cdot \text{H} \\ & \text{C} \cdot & \\ \text{H} \cdot & & \cdot \text{H} \end{matrix} \qquad \text{and} \quad \text{H} \cdot \text{H}$$

Acetylene. Methane. Hydrogen.
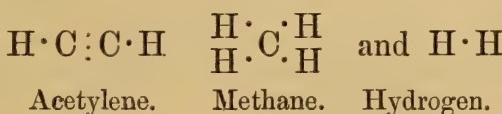
are produced. Of these, acetylene is the one that, on decomposition, emits almost all the light. Professor Lewes finds that, on attaining a situation where the temperature is sufficient, the acetylene resolves into carbon and hydrogen, which subsequently combine with oxygen ; and that in the brief interval one or both of them emit *more light than belongs to the temperature of that situation* ; in other words, that one or more electrons associated with Bb motions have been roused into great activity by the decomposition, and have time to radiate abundantly, probably a long time from the molecular standpoint, before either they have expended their

excess of energy, or the combination with oxygen takes place, whichever event comes first.

The summary of the results of this recent investigation have been here translated into molecular language, to serve as an example of the additional insight which we may already hope to gain into the chemistry of nature by adopting the molecular standpoint; and whenever the secret of the motions of electrons within molecules becomes known this insight will doubtless be vastly increased. Through the spectroscope we seem to be on the borderland of this great discovery.

Reference has been made to chemical reaction, friction, and the disruption of a crystal, as events which may bring into a state of activity some of the electrons associated with B*b* motions. Another event which seems to have this effect is the gaseous encounter between two molecules of the same kind. A suggestive experiment was made in the laboratory of the Royal Dublin Society, when Professor Emerson Reynolds, F.R.S., and the present author were engaged in examining the spectra of coloured vapours (Philosophical Magazine, July 1871, p. 41). We had examined the splendid absorption-spectrum of chlorochromic anhydride mixed with air. Here the encounters that the molecules of the vapour met with were most of them encounters with molecules of air, the minority only being encounters between molecules of the vapour. If the vessel containing the vapour be freed from air, the encounters between molecules of the vapour will be present in the same number as before, while all encounters between air and vapour will be absent. Hence we argued (for at that time we supposed the motions in the molecules to have been evoked by the undulation in the æther)*, that the molecules being less knocked about should produce a spectrum of lines that would be less diffuse. On trying the experiment, however, we found that the spectrum was sensibly the same as before. From this observation it would appear that the motions to which the spectrum is due are affected by the encounters between molecules of the

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* The amplitude of the B*b* motions which the undulation in the æther, if acting alone, can develop is apparently too small; and this is probably because, at this small amplitude, the transference of energy from B*b* motions to B*a* and A motions is inconspicuous. Where this is the case the ætherial undulation acting alone upon the gas cannot suffer any sensible amount of absorption. But the conditions are altogether different if some other agency produces an amplitude which can freely part with its energy by conduction, and which at the same time can be acted on by the æther in the direction which tends to keep the amplitude up. Under these circumstances there will be active withdrawal of energy from the æther, and an absorption-spectrum will result. This seems to be what happens in coloured gases.

[*Added September* 1895.—What seems a simpler and therefore more

vapour, and are uninfluenced by encounters between air molecules and vapour molecules. Hence they are due to something different from the mere kinetic energy of the collisions ; and this something may be, and probably is, that during the struggle between molecules of the same kind, a struggle which is a protracted struggle from the molecular standpoint, there occurs either always, or now and then, an interchange of some of the chemical atoms constituting the molecules. This, which is equivalent to two chemical decompositions, followed by two equivalent chemical combinations, must set the electrons concerned into a state of more or less activity.

This interchange of atoms during the encounters is presumably the source, not only of such absorption-spectra as that of chlorochromic anhydride, but also of the bright spectra seen in Plücker's tubes.

If the gas be monatomic, the spectrum is probably emitted only when the circumstances are such that two molecules can temporarily coalesce into a diatomic molecule during the encounter, and become dissociated when the encounter is over ; but in all cases where there is no ultimate change in the chemical constitution of the gas, its spectrum seems to be due to some event which is equivalent to equal and opposite chemical reactions having taken place during either all or some of the encounters.

An excellent way of helping us to appreciate the events with which we have to deal in molecular physics, is to conceive a model of them in which the durations shall all be enlarged 600 billions of times (6×10^{14}). This particular magnification is found to have special convenience attached to it*. If prolonged to this extent, the most rapidly recurring motions in nature that are *as yet* known to us, viz., those periodic events in a gas which give rise to the lines in its spectrum, would swing at rates comparable with the motions

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probable explanation has been suggested to me by Professor FitzGerald. It is that the electrons are sufficiently linked together through the æther to be but little affected by the A and B*a* events while on their side competent to influence such events, in the way described on p. 376. Under these circumstances the number of encounters might be increased by adding air, or otherwise, without perceptible effect on them ; while they, if susceptible of being excited by light in the way that phosphorescent bodies are, would act as carriers of energy from the æther to the A and B*a* events, thus causing absorption of light. It ought not to be impracticable to devise experiments which will determine with certainty which of the possible explanations is the real one.]

* Wave-lengths of rays of light are usually expressed as fractions of a micron, and pendulums beating the same fractions of a second represent the corresponding ætherial vibrations on the scale employed in the text.

of the limbs of animals, and would have about as great a range
from the swiftest of them to the slowest.   On the same
immense time-scale the duration of the journeys of the mole-
cules of ordinary air would average about one day each, while
the encounter which closes each journey may last some 20
minutes *.   The motions of the limbs of animals are able to
accomplish a good deal in a struggle lasting 20 minutes.   On
the same scale, the ten-thousandth of a second of time grows
to be an immense duration, extending to 1900 years.   The
number of struggles to be encountered by each molecule in
the ten-thousandth of a second is accordingly the same as the
number of days in the whole Christian Era, from the birth of
Christ down to the end of the present century.   If something
can be done during the 20 minutes that one of the struggles
may last, how great a task might be accomplished by such an
enormous succession of them.   It must be borne in mind, too,
that these encounters are not mere repetitions of one another,
but that each has its own definite incidents.   Moreover, all
this is what occurs in the experience of one individual molecule,
so that we must multiply it by something like a thousand

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* We may fill in this picture by combining a lengthening of distances
with the prolongation of the times.   A cubic millimetre, the volume of
a small pin's head, if each of its edges were magnified 10^{10} times, would
become almost as huge as the earth.   Under the same circumstances
molecules of air would be spaced at intervals averaging ten metres; and
700 metres would have become the mean distance to which they would
travel between their encounters.   On this great scale it would not be
inappropriate to use men or other animals to represent the individual
molecules—their hearts beating, their chests heaving, their limbs in
vigorous motion to represent the B or internal events.   And as to the mo-
tions with which the molecules of a gas dart about amongst one another,
these as they exist in common air would have become journeys as long
and of as various lengths as the streets of a great city, while the widths
of the streets may stand for the intervals at which the representatives of
the molecules are to be spaced asunder at starting.

In this model we have applied so much more magnification to time
than to space that all the velocities come out 60,000 times slower than in
nature.   Accordingly our animated molecules must be conceived of as
quietly gliding along the journeys they have to make between their
encounters; for the mean duration of a journey is to be a day, and the
average speed must accordingly be only half a metre per minute—on the
supposition that our model is to represent what occurs in gas as dense as
air and at its temperature and pressure.   It thus appears that we must
conceive them as requiring on the average about a quarter of an hour to
get past each house in the streets along which they have so slowly to
make their way.

A model of this kind is not without its use, if it were only as a means
by which we can gain a lively perception of how considerable the events
going on *within* the molecules may be when compared with the motions
of translation of the molecules.

millions, in order to sum up what may be accomplished by all the encounters of all the molecules within one cubic micron * of gas in the ten-thousandth part of a second, and that we may in some degree understand how it comes to pass that opportunity is afforded in nature for accomplishing work which requires rare collocations of conditions that can but seldom emerge. Such is Nature's real laboratory—events in inconceivable numbers, the whole phantasmagoria of these innumerable events changing every instant down to its minutest details with inconceivable rapidity, the changes in most cases kept within limits, but in some exploring every part of a wide range : it is thus that those wonderful operations are carried on, which issue in the astonishing results that lie everywhere in such profusion around us. We seem almost to get an obscure and partial glimpse of how, in organic nature, tasks of the most unlikely kind are accomplished, through the needful opportunities now and then turning up within each tiny speck of so Protean a material as protoplasm, a body of which the mutations have probably time-relations of the same order as those we have been endeavouring to illustrate, and whose activities are therefore more incessant, more various, and more complex, within every thousandth of a second, in every speck and corner of each living cell, than the mind can even conceive. It is very little man yet knows of what is going on abundantly about him in every stick and stone.

XXXI. *On the Cryoscopic Relations of Dilute Solutions of Cane-Sugar and Ethyl Alcohol. By* HARRY C. JONES[†].

THAT the van't Hoff[‡] equation $t = 0.02 \dfrac{T^2}{W}$ does not hold for the lowering of the freezing-point of water produced by the presence of a very small amount of such a non-electrolyte as cane-sugar, is indicated by the work of Arrhenius[§], Raoult[||], Loomis[¶], myself[**], and others. While the molecular lowerings for dilute solutions of several non-electrolytes as found by Loomis are less than the calculated, the

* There are 70 or 80 cubic microns in the volume of each of the small disks in human blood.

† Communicated by the Author.

‡ *Zeit. f. phys. Chem.* i. p. 497.

§ *Ibid.* ii. p. 495. || *Ibid.* ix. p. 343.

¶ *Ber. d. deutsch. chem. Gesell.* xxvi. p. 797.

** Phil. Mag. xxxvi. p. 465 (1893) ; *Zeit. f. phys. Chem.* xii. p. 642.

molecular lowerings as found by Arrhenius, Raoult, and myself, for the same concentrations of some or all of these compounds, are greater than the theoretical value. That more work on this problem was necessary was further shown by the fact, that no two of the observers above cited had been able to obtain the same results for even one non-electrolyte. It is, however, gratifying to know that with electrolytes our knowledge seems to be far more satisfactory. The dissociation of a comparatively large number of acids, bases, and salts, as calculated from Kohlrausch's conductivity-determinations* $\left(\alpha = \dfrac{\mu v}{\mu \infty} \right)$, agrees as well as could be expected with the dissociation of the same dilutions of these same compounds, as calculated from my results† from the lowerings of the freezing-point of water, ($\alpha = i - 1$ when the molecule dissociates into two ions, $\alpha = \dfrac{i-1}{2}$ when into three).

Noyes and Abbot‡ have recently shown that the dissociation of thallous chloride, sulphocyanate, and bromate, as calculated from solubility-experiments, agrees with the dissociation of these compounds as calculated from conductivity-results. In their words, "Die Löslichkeits und die Leitfähigkeitsmethode der Bestimmung der Dissociation auf die gleichen Resultate führen." The authors recognize that this conclusion is based on a small number of facts, only three compounds having been investigated, yet three which differ, chemically, very widely from one another. Noyes and Abbot conclude, "Die Verallgemeinerung dieses Resultates bezüglich anderer ähnlichen binären Salze, scheint daher berechtigt." We have then the three methods—conductivity, lowering of the freezing-point, and solubility—having to do with such widely different properties of the ions as the lowering of the freezing-point of the solvent, carrying electricity, and their mass action on each other's solubility, giving results for the number of ions present in any solution (the dissociation) which agree satisfactorily with one another. Some not inconsiderable difference appeared between my results and those of Kohlrausch for certain compounds§, but these seemed to have admitted of at least a rational explanation.

In the midst of the uncertain state of our knowledge as to the true lowerings produced by non-electrolytes, a paper

* Wied. *Ann.* xxvi. p. 161.
† Phil. Mag. xxxvi. p. 483 (1893); *Zeit. f. phys. Chem.* xii. p. 639.
‡ *Zeit. f. phys. Chem.* xvi. p. 136.
§ Phil. Mag. xxxvi. p. 483 (1893); *Zeit. f. phys. Chem.* xii. p. 639.

appeared from Nernst and Abegg*, which from its claims has doubtless aroused the interest of all who are studying such problems, and especially of those who are working directly along this line. Disregarding the unusual lack of courtesy which Nernst and Abegg have manifested towards some of those who have at least brought out the difficulties and discrepancies which exist in this field, which they have just entered, and subjecting their paper to a careful study, I am unable to see that they have accomplished *all* that is claimed in their communication. Some of the more prominent reasons for this conclusion will be given. Their correction-term introduced to eliminate errors from stirring &c. appears to me to involve the assumption that K for solutions is the same as for water, which assumption is gratuitous and unallowable.

Again, the experimental work itself, as judged by the apparatus and the results, seems to be far too inaccurate to be satisfactory where the quantities measured are so small, and where slight errors in the results might conceal the whole question under investigation.

The two series of measurements of the lowerings produced by solutions of sodium chloride, as made by Nernst and Abegg, differ for the same dilution somewhat more than 5 per cent. Why there should have been any difference is not apparent to me ; and still less is it apparent why apparatus and a method which did not yield concordant results for a compound which is as simple to deal with as sodium chloride should have been applied to a delicate problem with the non-electrolytes, which evidently can be solved only by accurate work with very refined methods.

The results of Nernst and Abegg with ethyl alcohol show a not inconsiderable rise in the molecular lowering with increase in dilution. To bring out this point more clearly their results are given.

Concentration.	Lowering.	Molecular Lowering.
0·0185	0·0365	1·97
0·0364	0·0685	1·88
0·0703	0·1307	1·86
0·1316	0·2432	1·85

The point made is not alone that the one value (1·97) is higher than the theoretical, but that the molecular lowering *increases* throughout the series, from the most concentrated

* *Zeit. f. phys. Chem.* xv. p. 680.

to the most dilute solution.   Had the series been extended to any very considerable dilution (say 0·005 n), with the same rate of increase molecular lowerings would have been found differing *unmistakably* from the calculated constant.   This can be seen most accurately by plotting the results in a curve.

While the correction-term for ethyl alcohol was small enough to be neglected, with cane-sugar it assumed considerable dimensions, amounting to 0°·006, where the quantity measured was only 0°·0277, being thus somewhat more than one fifth of the whole.   Unless a correction-term enjoys mathematical exactness, its introduction, when amounting to more than 20 per cent., would not tend to increase our confidence in the final result.   The results throughout with cane-sugar are not very convincing, being only very rough approximations to the theoretical value 1·87.   It further seems desirable to know how Nernst and Abegg assured themselves of the purity of the compounds which they employed, since one searches their paper in vain for evidence that this, the chemical side of the problem, has received any attention.

The experimental work of Nernst and Abegg as recorded in the paper in question *, as it appears to me, may be fairly summarized thus.   When measurements were made of the lowering of the freezing-point of water by dilute solutions of cane-sugar and ethyl alcohol, and when the former were corrected by a term amounting to as much as 22 per cent. of the quantity measured, and the latter not corrected at all, values were obtained for molecular lowerings which were not more than 6 per cent. greater (1·97 for ethyl alcohol) than the theoretical, 1·87; nor more than 7·5 per cent. less (1·73 for cane-sugar).   From their results the authors concluded that non-electrolytes give theoretical results.

A valuable suggestion, however, which can be tested experimentally, has been made in this paper by Nernst and Abegg; and the object of the work herein described is to study the effect of the temperature of the freezing-mixture on the results.   The authors thought that the difference between the results found by the different experimenters, working with cane-sugar for example, was caused by the use of freezing-mixtures of different temperatures.   How far this was of influence will appear from the following work.

In this investigation cane-sugar solutions were used for the most part, since with this compound so many have worked and have obtained such widely different results; and, further, it was with this substance that the above-mentioned correction

* *Zeit. f. phys. Chem.* xv. p. 680.

was considerable. A few solutions of ethyl alcohol were also investigated under the same conditions as those employed for cane-sugar. To the results obtained for this compound Nernst and Abegg introduced no correction.

The cane-sugar used was a beautifully crystallized sample, which was shown by analysis to be free from inorganic matter and from dextrose. A one-half normal solution was prepared each day from a carefully dried specimen, and in no case was a solution used which had been made up more than twenty-four hours.

In the first series of measurements, a freezing-mixture of such temperature was employed that the air-bath surrounding the solution whose freezing-point was to be determined was at no time colder than $-5°$. The apparatus used was essentially that employed hitherto by myself[*], and the method of work that already described. The stirring was carried on very slowly and regularly, and a comparatively large amount of ice was allowed to separate from the solution before the reading was taken on the thermometer.

First Series of Measurements.

$$C_{12}H_{22}O_{11} = 342\cdot11.$$
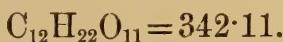
Grams in litre.	Normal.	Lowering found.	Gram-mol. Lowering.
7·775	0·0227	0·0493	2·17
15·550	0·0455	0·0961	2·11
23·325	0·0682	0·1397	2·05
31·100	0·0909	0·1792	1·97

A second series was then made with cane-sugar, where the air-bath surrounding the solution was never colder than $-4\frac{1}{2}°$. The solutions were all stirred very gently, and considerable time was allowed for the thermometer to reach a point of equilibrium.

Second Series of Measurements.

Grams in litre.	Normal.	Lowering found.	Gram-mol. Lowering.
7·775	0·0227	0·0497	2·19
15·550	0·0455	0·0958	2·11
23·325	0·0682	0·1399	2·05
31·100	0·0909	0·1796	1·98

The gram-molecular lowerings found in the two series

[*] *Zeit. f. phys. Chem.* xi. p. 532.

agree to within experimental errors, and are in all cases much greater than the theoretical value.

These results do not differ to any considerable degree from those which were found when cane-sugar was first studied[*].

It was then decided to make some determinations in which the temperature of the freezing-mixture differed from the freezing-point of the solution under investigation by an amount so small that the latter only just froze. The freezing-mixture used was prepared from alum and ice. But on account of the large volume of the solution used (1100 cubic centim.) and the large air-space which separated this from the freezing-mixture, it was found that the time required to cool the solution even $0°.5$ was so great as to be impracticable. A freezing-mixture which answered the requirements satisfactorily was prepared as follows :—An intimate mixture was made of powdered ice and alum, then a very small amount of common salt was added. This mixture, when used in my apparatus, gave a temperature in the air-bath around the solution of never more than $0°.5$, and usually less than $0°.4$, lower than the freezing-point of the solution. The solution was cooled down to within a fraction of a degree from its freezing-point in a colder bath, and was then placed in the bath surrounded by the mixture just described. All determinations were thus made with a freezing-mixture from $0°.3$ to $0°.4$ colder than the freezing-point of the solution.

The details of the procedure for a single determination were as follows :—1100 cubic centim. of distilled water, cooled nearly to zero, were placed in the glass vessel C[†], and cooled to within a tenth of a degree of zero in a bath surrounded by a mixture of salt and ice. The glass vessel was then placed in the metallic vessel B, which was surrounded by a freezing-mixture of ice and alum prepared as above described, and the water stirred gently until it had cooled down to $-0°.6$ or $-0°.7$. A small piece of pure ice was then thrown into the water, which brought about at once a separation of ice throughout the liquid. The stirring during the formation of the ice was accomplished by a very gentle movement of the stirrer, which with the form employed was found to be amply sufficient. In this manner the liberation of heat in such quantities that the thermometer was affected by it before it could meet the ice was prevented, as was shown by the fact that when the thermometer had reached a constant point, stirring for a long time failed to change the reading a perceptible amount. Thus was avoided experimentally a comparatively large and

[*] *Zeit. f. phys. Chem.* xii. p. 642; and Phil. Mag. xxxvi. p. 486 (1893).
[†] *Zeit. f. phys. Chem.* xi. p. 532.

necessarily uncertain correction to eliminate the effect of stirring. The water containing the ice was allowed to remain in the bath until the thermometer rose to a point at which it stood constant for from five to ten minutes. About half an hour elapsed from the time that the first ice separated until the final reading was taken on the thermometer. A second determination of the freezing-point of the water was then made, just as the first had been. The thermometer used in all of this work was the one already described* as of the Beckmann type, and divided directly into *thousandths* of a degree. Knowing the freezing-point of the water on the thermometer, the vessel containing it was removed from the bath, the ice melted, and then a measured volume of the water pipetted off. An equal volume of a one-half normal sugar solution, which had been prepared only a few hours, was then added. This new dilute solution of sugar was thoroughly stirred, and its freezing-point determined in all respects as that of the water, as described above. The time required for a complete determination of the lowering of the freezing-point of water produced by a sugar solution being from 12 to 16 hours, it is therefore evident that, under the conditions employed, only one determination could be made in a day.

Each morning a new volume of water was used, its freezing-point ascertained, and a more or less concentrated sugar solution prepared from it and the freezing-point determined as described. The precaution was taken to prepare the one-half normal sugar solution from some of the same specimen of water whose freezing-point was determined on the day that this solution was used.

The Results.

Grams in litre.	Normal.	Lowering found.	Gram-mol. Lowering.
3·8875	0·01136	0·0251	2·21
7·775	0·0227	0·0475	2·09
15·550	0·0455	0·0915	2·01
23·325	0·0682	0·1333	1·95
31·100	0·0909	0·1734	1·91

These results show by comparison with those obtained when a much colder freezing-mixture was used, that the temperature of this mixture is to be considered in the case of such a substance as cane-sugar. The molecular lowerings here are *throughout* somewhat lower than the preceding series. To test the measurements a duplicate series was made.

* *Zeit. f. phys. Chem.* xi. p. 532 (Q).

Duplicate Series with Cane-Sugar.

Grams in litre.	Normal.	Lowering found.	Gram-mol. Lowering.
3·8875	0·01136	0·0247	2·174
7·775	0·0227	0·0481	2·119
15·550	0·0455	0·0919	2·02
23·325	0·0682	0·1327	1·946
31·100	0·0909	0·1737	1 911

The two series agree satisfactorily throughout.

In these determinations a large volume of solution (1100 cub. centim.) has been employed, diminishing thus very greatly the effect of disturbing influences from without. A freezing-mixture was employed which was only a few tenths of a degree colder than the freezing-point of the solution. The stirring was carried out so gently that errors from this source could not have assumed any appreciable dimensions, and yet the molecular lowerings found are *far above the theoretical value.* I can hardly conceive that anyone can now claim with any degree of probability, that the cause of the difference between the observed and calculated values is to be found in the very cold freezing-mixture employed, or in the heating of the solution by stirring, or that equilibrium was not established in the solution, in consideration of the amount of ice which was present, and the time which was allowed for the equilibrium to establish itself.

That somewhat lower values had been found for cane-sugar, when a less vigorous freezing-mixture was used, led me to investigate some other non-electrolyte,—ethyl alcohol was chosen. Absolute alcohol was prepared by treating 95 per cent. alcohol with lime, distilling, and allowing the product to stand over anhydrous copper sulphate ($CuSO_4 . H_2O$) for several months. From a normal solution of the alcohol, the more dilute solutions were prepared when needed. The determinations were carried out exactly as with cane-sugar. The temperature of the freezing-mixture was only a few tenths of a degree lower than the freezing-point of the alcoholic solutions.

Results with Ethyl Alcohol.

$$C_2H_6O = 46·03.$$
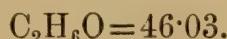
Grams in litre.	Normal.	Lowering found.	Gram-mol. Lowering.
1·0461	0·0227	0·0476	2·10
2·0923	0·0455	0·0911	2·00
3·1384	0·0682	0·1335	1·96
4·1845	0·0909	0·1745	1·92

Change in the freezing-mixture produced thus very nearly

the same effect on the lowering produced by ethyl-alcohol solutions as on that of cane-sugar. Here also the molecular lowerings found are considerably higher than the theoretical, 1·87.

A comparison of the results which I have found under these conditions for cane-sugar with those obtained by Raoult * for this compound, will show that the two series agree well for the more dilute solutions, while my results are somewhat lower for the more concentrated. Since this work was undertaken, Raoult has kindly informed me that he has repeated his work with cane-sugar, using an improved cryoscope †, constructed so as to prevent direct radiation from the freezing-mixture to the bulb of the thermometer. This was accomplished by interposing a sheet of platinum, which served at the same time as a stirrer. Results were obtained which agree well with those found earlier by him‡, strengthening him in the belief that the molecular lowerings of cane-sugar in dilute solution are greater than the calculated, and that this increases with the dilution. I take the liberty to quote a line from the letter of this distinguished authority, on problems of this character :—" Pour conclure, je reste convaincu que les abaissements moléculaires de l'alcool en dissolution aqueuse, comme ceux du sucre, deviennent de plus en plus supérieurs à la valeur normale à mesure que les liqueurs deviennent plus étendues." And who deserves to be heard in reference to the freezing-point method if it is not Raoult ? since it was he who showed, by his extended investigations §, the significance of " molecular lowerings," and gave us in this method the means of determining the molecular weights of substances in solution ‖. What has been done subsequently in this line either bears an evident theoretical relation to the work of Raoult, or consists in devising better apparatus and more accurate methods for carrying out the measurements.

To summarize :—In the above tables are recorded the results of measurements of the freezing-point lowerings of water by solutions of two non-electrolytes. The work was not extended to dilutions greater than 0·01 normal, since for greater dilution the experimental errors necessarily increase. But for the dilutions used molecular lowerings were found, which rise very appreciably above the theoretical value. Methods of work were employed which seem to eliminate experimental errors arising from too cold a bath, too vigorous stirring, or a failure to establish equilibrium in the solution, and still the

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* *Zeit. f. phys. Chem.* ix. p. 343.
† *Revue Scientifique*, Sept. 15th, 1895.
‡ *Zeit. f. phys. Chem.* ix. p. 343.
§ *Compt. Rend.* xciv. p. 1517; xcv. pp. 188, 1030.
‖ *Compt. Rend.* ci. p. 1056.

results were too high. Thus the problem stands. In the light
of this new work, I do not see a sufficient justification for the
conclusion that non-electrolytes, in fairly dilute solution,
give lowerings which conform to the equation $t = 0.02 \dfrac{T^2}{W}$. A
very satisfactory agreement for more concentrated solutions
has been shown by others and confirmed by myself [*]. That
such a discrepancy should exist for very dilute solutions does
not appear to me to be *à priori* impossible. Take the case of
dilute gases. The law of gaseous expansion with temperature
is fairly well established as an approximate expression of the
truth, yet Ramsay and Baly [†] have recently shown that it
does not hold when the gases become very dilute. The
coefficient of expansion for dilute gases is not a constant, but
is sometimes greater, and at times less, than the normal. To
illustrate this, I give a few of their results :—

Hydrogen.		Oxygen.		Nitrogen.	
Pressure. millim.	Coef. Exp.	Pressure. millim.	Coef. Exp.	Pressure. millim.	Coef. Exp.
3·47	$\dfrac{1}{273\text{--}74}$	5·1	$\dfrac{1}{260}$	5·3	$\dfrac{1}{304}$
0·096	$\dfrac{1}{297}$	1·4	$\dfrac{1}{233}$	0·8	$\dfrac{1}{331}$
0·077	$\dfrac{1}{300\cdot5}$	0·07	$\dfrac{1}{240}$	0·6	$\dfrac{1}{355}$ to $\dfrac{1}{377}$

If dilute gases, then, do not obey the expansion law, to
which more concentrated gases conform, might it not be that
dilute solutions of non-electrolytes do not conform to the
law of the lowering of the freezing-point which holds for
more concentrated solutions of the same substances? It
seems to me that the analogy is at least suggestive, since,
thanks to van't Hoff, we know that solutions resemble gases
in a striking manner.

However this may be, I believe the question must be
settled by direct experiment, rather than by the introduction
of doubtful corrections, which, when applied to the experi-
mental results, give values which lie somewhere in the neigh-
bourhood of the calculated.

The point raised by Wildermann [‡], in connexion with the
use of my thermometer, that when the ice separated from the
water, a layer formed around the bulb, seemed to be worth
testing again. I could not think that this was possible, since
in earlier work this point had received attention, yet experi-

[*] *Zeit. f. phys. Chem.* xii. p. 653; *Phil. Mag.* xxxvi. p. 494 (1893).
[†] *Phil. Mag.* xxxviii. p. 301 (1894).
[‡] *Zeit. f. phys. Chem.* xv. p. 358.

ments were carried out again to test the suggestion, with water, with dilute, and with concentrated solutions. The result was, as I convinced myself and others, *that not a trace of ice ever froze to the bulb of the thermometer under any condition.*

When the thermometer was quickly removed from the water, a few snow-like flakes came up with it. These were in no sense attached to the bulb, but *floated off at once* with the liquid which had adhered to it. It must then be stated emphatically that this assumption of Wildermann, as far as the work with my thermometer is concerned, receives absolutely no support from the experimental facts*.

Chemical Laboratory,
Johns Hopkins Univ., June 1895.

XXXII. *Notices respecting New Books.*

An Introduction to Chemical Crystallography. By ANDREAS FOCK, *Ph.D., translated and edited by* WILLIAM J. POPE, *with a preface by* N. STORY-MASKELYNE, *M.A., F.R.S.* Pp. 189 & xvi. 8vo. (Oxford: Clarendon Press. 1895.)

THE importance of a knowledge of crystallography to all workers in the fields of chemical research has not hitherto been sufficiently recognized either at home or abroad. It is therefore an encouraging sign of the times that this little book has been prepared for the use of students in the Central Technical College, and also in order to call the attention of chemists to the important relations which exist between crystalline form and chemical composition. Mr. Pope deserves accordingly the gratitude of all who are interested in the progress of chemistry in this country for his excellent translation of Dr. Fock's *Einleitung in die chemische Krystallographie.*

The book is divided into twenty-five short chapters: the first fifteen of these deal with the nature of crystals, solutions, and double salts, the growth of crystals and their production in the laboratory.

The consideration of the relations between chemical composition and crystalline form begins on page 84 with an historical sketch of isomorphism, and in the chapters which follow the properties of

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* In a recent publication (Phil. Mag. xl. p. 120, 1895) Wildermann has quoted Ostwald as saying that my freezing-point method required further development (in Wildermann's hands), "because the results obtained for non-electrolytes by this method do not agree with the fundamental generalizations of the modern Theory of Solutions."

It is difficult for a student of the great Thinker to conceive of him judging results by any theory, thus taking a position which accords priority to the theory, rather than to the experimental data on which it is founded, and by which it must be tested.

It also appears to me that it would have been more in accord with scientific custom had Dr. Wildermann granted Ostwald the opportunity of offering his own criticism, which, had it ever appeared first-hand, would have differed from the second-hand version in this, that it would have been accompanied by the legitimate reasons on which it was based.

isomorphous substances, the nature of physical isomerism, and morphotropy are discussed. Many of these chapters, especially the historical ones and those dealing with isomorphism, are highly interesting, and the author and translator have kept in touch with the important recent work of Muthmann, Retgers, Roozeboom, and Tutton, so that on the whole the book is well calculated to afford the student a glimpse into a new and but little explored territory. Within the compass of 190 short pages it is, however, impossible to deal adequately with all branches of the subject, and much of the book, particularly the first half of it, is open to criticism on the ground of extreme sketchiness; too often also the author has failed to distinguish between the essential and the unimportant, and the student must be on his guard against accepting as proven dogmatic statements unsupported by evidence.

The inaccuracies of the German edition have for the most part been corrected. It is, however, unfortunate that the axial ratios of meta-dinitrobenzene should still be assigned to tri-nitrobenzene at the end of the account of Friedländer's work introduced to illustrate the sort of aid the organic chemist may obtain from the crystallographer. The chemist will, we fear, find at first sight some difficulty in tracing the obvious crystallographic relations which he is told exist, and will hardly be sufficiently impressed with the value of such researches.

The author's preface to the German edition is not translated, its place being apparently taken by an introduction from the pen of Professor Story-Maskelyne, in which the objects of the book are set forth, and attention called to the results of van't Hoff's work, and to the importance of the study of mixed crystals and double salts.

Paper and printing leave nothing to be desired, and in spite of defects this little book ought to be in the hands of all advanced students of chemistry, and should stimulate many to take an interest in a fascinating subject, rich in problems awaiting solution.

XXXIII. *Proceedings of Learned Societies.*

GEOLOGICAL SOCIETY.

[Continued from p. 320.]

June 19th, 1895.—Dr. Henry Woodward, F.R.S., President, in the Chair.

THE following communications were read:—

1. 'On the Occurrence of Radiolaria in Chalk.' By W. Hill, Esq., F.G.S., and A. J. Jukes-Browne, Esq., B.A., F.G.S.

2. 'The Crush-Conglomerates of the Isle of Man.' By G. W. Lamplugh, Esq., F.G.S.; with an Appendix by W. W. Watts, Esq., M.A., F.G.S.

The Skiddaw Slates of the Isle of Man have everywhere undergone intense shearing, and on the north-west side of the main stratigraphical axis actual disruption of the bedding with the resultant formation of breccia or crush-conglomerate on a large scale has taken place. This structure attains its widest develop-

ment on the north side of the central valley, though it is noted on a more limited scale in a few localities farther south. It is well exposed in the cliffs 3 miles north of Peel, but the finest sections are in the interior in Sulby Glen, where the structure has a thickness of some hundreds of feet, and runs continuously about north-north-east for 5 miles, with a probable extension southward for 3 miles farther, and also eastward for other 4 miles. It is usually flanked by gritty flags on one side, and by dark clay-slates on the other. It is affected by a strain-slip cleavage later than the brecciation, and several igneous dykes which intersect it are affected by the same cleavage, though not by the brecciation-movement.

East of Sulby Glen the structure extends towards Ramsey, at first in a horizontal spread over a mile in width, and afterwards in a series of comparatively narrow subparallel bands, and it is suggested that we are dealing here with the emergence of a deformed plane. The structure is continued eastward into the hill overlooking Ramsey, beyond which it is cut off by the sea. In this locality, as elsewhere, the sections show the gradual smashing into fragments of highly contorted strata until every trace of the original bedding is lost, and a 'crush-conglomerate' with lenticular and partly rounded inclusions is formed.

The rocks described in Mr. Watts's Appendix are grouped in four classes. Firstly, the grits and slates which have been crushed but have not been converted into crush-conglomerates; secondly, the crush-conglomerates themselves, and the fragments which they contain; thirdly, the dykes of decomposed dolerite (greenstone) and fresh later dolerite which penetrate the conglomerate; fourthly, a portion of the crush-conglomerate metamorphosed by these intrusions.

The chief point of interest is brought out by the examination of the fragments in the conglomerate. All stages of crushing may be traced, until the grit-fragments have a structure which is a mere miniature of the crush-conglomerate itself; that is to say, if the crush-conglomerate be regarded as made of 'fragments' of hard rocks enclosed in crushed 'matrix' of soft rocks, a host of intermediate varieties with varying resistances will occur. Whether any particular one of these varieties shall pass into 'fragments' or 'matrix' under the crushing will depend upon the amount of the crushing force and upon the association (paragenesis) of the material brought together to be crushed.

XXXIV. *Intelligence and Miscellaneous Articles.*

A SIMPLE METHOD OF DETERMINING THE DURATION OF TORSIONAL OSCILLATIONS. BY R. W. WOOD.

IN what follows I wish to describe a method by which the time of torsional oscillations may be conveniently observed, for instance that of a magnet in determining the horizontal intensity of terrestrial magnetism. The usual methods labour under the drawback that the watch and the oscillating body cannot be simultaneously observed. In the present method the watch is brought into the field of view of the telescope with which the vibrations are observed.

A small light mirror is fastened with wax to the vibrating body in the usual way, and a telescope is sighted at a distance of about two metres. Between the telescope and the mirror is fixed near the latter a thin plane glass, silvered by means of Böttger's solution, making an angle of 45° with the vertical. This must reflect more light than it transmits.

A watch is placed on a table below the mirror so that its image reflected from the silvered surface is distinctly visible in the field of view of the telescope. The watch must be brightly lighted by a lamp, and another lamp so placed near the telescope that its rays passing through the transparent coating are reflected by the small mirror into the telescope. On looking through the telescope after the body has been made to oscillate, we see the second-hand strongly magnified, while at each oscillation the small vibrating mirror gives a short flash in the field of view. The image of the second-hand moves in the opposite direction to the hand itself. By following the motion of the hand it is easy to accurately determine the time of the flash to a quarter of a second. If the oscillations are rapid, it is of course more convenient only to observe the time of every fifth or tenth oscillation. After a few observations we know when the following is to be expected, and by fixing the eye on the division of the dial where the second-hand will be at the moment of the flash, it is possible to determine the time to within a quarter of a second. We soon get accustomed to the backward motion of the index, and the reading is as easy as the ordinary one.

Instead of the semitransparent silver mirror an ordinary opaque plane mirror may be used (metal of course is best), if it is so arranged that the mirror on the oscillating body is visible just above or below its edge.—Wiedemann's *Annalen*, No. 9, 1895.

ON THE INCONSTANCY OF THE POTENTIAL REQUIRED FOR A SPARK. BY G. JAUMANN.

The author summarizes as follows the results of his investigation:—

I. Sparks alter the path through which they pass; strong ones in an unfavourable sense, and weak ones often in a favourable sense. The path spontaneously recovers from this after-action in the course of some hours.

II. By avoiding the smallest variations of force very high potentials may be obtained.

III. When the conditions for a discharge are not quite satisfied, the discharge takes place after a delay of a few seconds to several minutes. During this retardation there is a preliminary process of discharge which itself is no real discharge.

IV. During this retardation the exciting influence of variations of force can be demonstrated in an incontestable manner.

V. A moderate variation of force does not produce the spark at once, but only after 0·1–5 seconds. It only accelerates the preliminary process and shortens therefore the retardation.—Wiedemann's *Annalen*, No. 8, 1895.

XXXV. *On the Properties of a Mixture of Liquids.* By R. A. LEHFELDT, *B.A., B.Sc., Demonstrator at Firth College, Sheffield*[*].

(i.) *Deduction of a Thermodynamic Relation.*

WHEN a mixture of two liquids is allowed to evaporate, interesting questions arise on the relation between the composition of the liquid and the composition of the vapour rising from it ; and the relations of each to the pressure of the vapour. There is, unfortunately, very little experimental evidence on either of these points, particularly on the composition of the vapour. It is possible, however, by thermodynamic reasoning, to obtain a relation between the quantities above mentioned, and so make experimental data on one point supply the lack of information on another.

When equilibrium exists between two bodies, the thermodynamic potential of the whole must be unchanged by any small variation of the system ; and if the two bodies are a liquid and its vapour, this condition may be applied to the change involved in the conversion of a small amount of the one into the other. Now suppose a mixture of two liquids A and B contained in a vessel in the upper part of which are two cylinders, with pistons ; and let the lower end of the cylinders be separated from the vessel by two semipermeable membranes, of which one lets only the vapour of A pass ; the other only vapour of B. Then by allowing the first piston to

[*] Communicated by the Author.

rise we may evaporate a little of A without altering the quantity of vapour of B present, nor the total pressure on the liquid : similarly, by raising the second piston we may evaporate B alone.

Let Φ be the thermodynamic potential of the liquid,

Φ' „   „   „   of the vapour ;

m and n the masses of A and B present as liquid,

m' and n' „   „   „   vapour.

Then the conditions of equilibrium are that

and

$$\frac{\partial\Phi}{\partial m}\,\delta m + \frac{\partial\Phi'}{\partial m'}\,\delta m' = 0, \left.\begin{array}{c} \\ \\ \\ \end{array}\right\} \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$\frac{\partial\Phi}{\partial n}\,\delta n + \frac{\partial\Phi'}{\partial n'}\,\delta n' = 0;$$

but as $\delta m = -\delta m'$ and $\delta n = -\delta n'$, we have

$$\frac{\partial\Phi}{\partial m} = \frac{\partial\Phi'}{\partial m'}, \left.\begin{array}{c} \\ \\ \\ \end{array}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

$$\frac{\partial\Phi}{\partial n} = \frac{\partial\Phi'}{\partial n'}.$$

We shall endeavour to evaluate the thermodynamic potential of the vapour ; to do this we assume that each of the two constituents of the vapour behaves as a perfect gas, and that the two constituents have no mutual action. We may then set the potential of the vapour equal to the sum of the potentials that each constituent would possess if it existed alone under the same temperature, and a pressure equal to its partial pressure in the mixture. We will express the specific potential of a simple liquid by $\phi(A, p, T)$, where A denotes the substance, p the pressure, and T the temperature ; and by $\phi'(A, p, T)$ that of the vapour. The second of the above assumptions may then be expressed algebraically by saying

$$\Phi' = m'\phi'(A, p_A, T) + n'\phi'(B, p_B, T), \quad . \quad . \quad . \quad (3)$$

where p_A, p_B are the partial pressures.

For the liquid we cannot make a similar assumption, we therefore put

$$\Phi = m\phi(A, p, T) + n\phi(B, p, T) + (m+n)f\left(A, B, \frac{m}{n}, p, T\right), \quad (4)$$

where p is the total pressure $(p = p_A + p_B)$, and f is a quantity expressing the mutual action of the two liquids ; it is a function of m/n, which we will write q, and its value is the subject of the investigation.

We may now write (2) as

$$\phi(A, p_A, T) + f(A, B, q, p, T) + (m+n)\frac{\partial}{\partial m}f(A, B, q, p, T) = \phi'(A, p_A, T),$$

$$\phi(B, p, T) + f(A, B, q, p, T) + (m+n)\frac{\partial}{\partial n}f(A, B, q, p, T) = \phi'(B, p_B, T);$$

or writing $f(A, B, q, p, T)$ as f for short, and transforming to q as the independent variable,

$$\left.\begin{array}{c} \phi(A, p, T) + f + (q+1)\dfrac{\partial f}{\partial q} = \phi'(A, p_A, T), \\[2mm] \phi(B, p, T) + f - q(q+1)\dfrac{\partial f}{\partial q} = \phi'(B, p_B, T). \end{array}\right\} \quad . \quad (5)$$

Now the thermodynamic potential of a perfect gas may be expressed in the form

$$\phi'(A, p_A, T) = \phi'(A, p_0, T) + \frac{RT}{A}\log\frac{p_A}{p_0},$$

p_0 being any other pressure, R the gas constant, and A the molecular weight of the gas. Take for standard pressure the saturation pressure of the pure vapour at the temperature considered. Let this be π_A, π_B for the two substances. Then

$$\left.\begin{array}{c} \phi(A, p, T) + f + (q+1)\dfrac{\partial f}{\partial q} = \phi'(A, \pi_A, T) + \dfrac{RT}{A}\log\dfrac{p_A}{\pi_A}, \\[2mm] \phi(B, p, T) + f - q(q+1)\dfrac{\partial f}{\partial q} = \phi'(B, \pi_B, T) + \dfrac{RT}{B}\log\dfrac{p_B}{\pi_B}. \end{array}\right\} (6)$$

But the thermodynamic potential of a liquid varies exceedingly little with pressure : so we will assume that

$$\phi(A, p, T) = \phi(A, \pi_A, T) ;$$

and the latter is equal to $\phi'(A, \pi_A, T)$, for liquid and vapour are in equilibrium at that temperature and pressure. Hence

$$\left.\begin{array}{c} f + (q+1)\dfrac{\partial f}{\partial q} = \dfrac{RT}{A}\log\dfrac{p_A}{\pi_A}, \\[2mm] f - q(q+1)\dfrac{\partial f}{\partial q} = \dfrac{RT}{B}\log\dfrac{p_B}{\pi_B}. \end{array}\right\} \quad . \quad . \quad . \quad (7)$$

From (7) we obtain by addition and subtraction,

$$\frac{\partial f}{\partial q} - \frac{1}{(q+1)^2}\frac{RT}{A}\log\frac{p_A}{\pi_A} + \frac{1}{(q+1)^2}\frac{RT}{B}\log\frac{p_B}{\pi_B} = 0, \quad . \quad (8)$$

and

$$f - \frac{q}{q+1}\frac{RT}{A}\log\frac{p_A}{\pi_A} + \frac{1}{q+1}\frac{RT}{B}\log\frac{p_B}{\pi_B} = 0. \quad . \quad . \quad (9)$$

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We will now introduce the symbols t for the ratio of the quantities of vapour, and s for the ratio of numbers of molecules present in the vapour. So that

$$t = \frac{m'}{n'}, \qquad s = \frac{B}{A}\frac{m'}{n'} = \frac{B}{A}t,$$

and

$$p_A = \frac{s}{s+1}p, \qquad p_B = \frac{1}{s+1}p.$$

Making these substitutions, differentiating (9) with respect to q, and subtracting (8) from it, we get

$$\frac{q}{q+1}\frac{RT}{A}\left\{\frac{1}{s(s+1)}\frac{\partial s}{\partial q} + \frac{1}{p}\frac{\partial p}{\partial q}\right\}$$

$$- \frac{1}{q+1}\frac{RT}{B}\left\{\frac{1}{s+1}\frac{\partial s}{\partial q} - \frac{1}{p}\frac{\partial p}{\partial q}\right\}; \quad . \quad . \quad (10)$$

or

$$\left(\frac{q}{As(s+1)} - \frac{1}{B(s+1)}\right)\frac{\partial s}{\partial q} + \left(\frac{q}{A} + \frac{1}{B}\right)\frac{1}{p}\frac{\partial p}{\partial q} = 0,$$

or

$$\left(\frac{Bq}{s(s+1)(Bq+A)} - \frac{A}{(s+1)(Bq+A)}\right)\frac{\partial s}{\partial q} + \frac{1}{p}\frac{\partial p}{\partial q} = 0,$$

or

$$\left(\frac{Bq}{Bq+A} - \frac{s}{s+1}\right)\frac{1}{s}\frac{\partial s}{\partial q} + \frac{1}{p}\frac{\partial p}{\partial q} = 0. \quad . \quad . \quad (11)$$

This, then, is the thermodynamic relation connecting p, q, and s. Experiments may give the vapour-pressure p as a function of the composition q of the liquid ; or the composition s of the vapour as a function of q. But if only one of these data exist, the equation gives the means of finding the other.

Equation (11), however, is not integrable in general : to make it integrable it is necessary to assume some particular relation between s and q. It follows, then, that if the form of the function s is known p can be calculated : but a knowledge of p does not suffice to calculate s.

(ii.) *Résumé of Experimental Data.*

Several physicists have measured the vapour-pressure over a mixture of two liquids whose volatility is comparable. The best measurements are, firstly, by Wüllner*, whose object was chiefly to investigate the variation of the vapour-pressure with temperature. The liquids he used were (i) water

* Pogg. *Ann.* cxxix. p. 353 (66).

and alcohol, (ii) alcohol and ether, (iii) ether and carbon disulphide. Unfortunately for our present purpose only the second and third of these can be regarded as a typical mixture, for water is anomalous in many of its properties.

Secondly, Konowalow[*] has published measurements of mixtures of water with methyl, ethyl, propyl, and isobutyl alcohols, and formic, acetic, propionic, and butyric acids, which illustrate well the different behaviour of completely and incompletely miscible liquids.

On the other hand, I am not aware of any measurements of the composition of the vapour rising from a mixture of liquids except those of F. D. Brown[†], who considered the point in connexion with fractional distillation. He used carbon disulphide and benzene; but as his method was to determine the composition of successive fractions in a distillation at constant pressure, he does not give a table of values of s as a function of q at any one temperature, as is required for our equation (11). He states, however, a general conclusion as to the composition of the vapour, which may be applied to equation (11), enabling us to integrate it, and his experimental numbers will then suffice to test the accuracy of the integral equation to a certain extent.

(iii.) *Integration of the Thermodynamic Relation, in particular Cases.*

F. D. Brown states that t is a constant multiple of q, where (as above) t expresses the ratio of the masses of the two substances in the vapour, q in the liquid. This generalization is confessedly only an approximate one ; and, further, without loss of accuracy the multiple may be taken as the ratio between the saturation-pressures of the two substances. That is,

$$t = kq;$$

or appproximately,

$$t = \frac{\pi_A}{\pi_B} q.$$

We proceed to show that according to our theory, if k is a constant it must have the value $\dfrac{\pi_A}{\pi_B}$.

Let
$$t = kq, \quad \text{then} \quad s = \frac{B}{A} kq, \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (12)$$

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[*] Wied. *Ann.* xiv. pp. 34–51, 219–225 (81).
[†] Journ. Chem. Soc. xxxv. p. 547 (79).

and (11) becomes

$$\left(\frac{Bq}{Bq+A} - \frac{Bkq}{Bkq+A}\right)\frac{1}{q} + \frac{1}{p}\frac{\partial p}{\partial q}=0, \quad . \quad . \quad (13)$$

the integral of which is

$$\log\left(q+\frac{A}{B}\right) - \log\left(q+\frac{A}{Bk}\right) + \log p = \text{const.}$$

We have, however, the two conditions that when $q=0$, $p=\pi_B$, and when $q=\infty$, $p=\pi_A$, hence we can evaluate both k and the integration constant, and we get

$$\frac{Bq\pi_A + A\pi_B}{Bq+A} = p, \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

and

$$k = \frac{\pi_A}{\pi_B}. \quad . \quad . \quad . \quad . \quad . \quad (15)$$

As the ratio between the partial pressures of the vapours is in this case $s = \frac{B\pi_A}{A\pi_B}q$, it is clear that the two terms of (14) represent the two partial pressures respectively, or

$$p_A = \frac{Bq}{Bq+A}\pi_A, \quad p_B = \frac{A}{Bq+A}\pi_B.$$

This result can be tested by Brown's table (*loc. cit.* p. 561), in which are given the boiling-points of various mixtures of benzene and carbon disulphide: using the vapour-pressures of the pure substances at the temperature of this boiling-point, the calculated value of p should be 760 millim. This is not the case: thus at $50°$ C. p works out to 713 millim. It is probable therefore that Brown's generalization is not sufficiently close an approximation for our purpose.

Guided by this result, we have, then, to choose some other probable function for t and s. It must satisfy these conditions: 1st, when only one substance is present in the liquid, only the same can be present in the vapour, so that

$$\text{when } q=0 \quad t=0,$$

$$\text{when } q=\infty \quad t=\infty;$$

2nd, if t is any function of q then $1/t$ must be a similar function of $1/q$, for obviously it can make no difference which of the two substances we choose for A and which for B. The simplest function that satisfies these conditions is $t=kq^r$, where k and r are constants.

Let us then substitute $s = \dfrac{B}{A} kq^r$ in equation (11) and integrate: we have now in all three constants (including the one introduced by integration), and two boundary conditions ($p = \pi_B$ when $q = 0$, $p = \pi_A$ when $q = \infty$), so that one constant remains to be determined by experiment.

Equation (11) becomes

$$\frac{Br}{Bq+A} - \frac{Bkrq^{r-1}}{Bkq^r+A} + \frac{1}{p}\frac{\partial p}{\partial v} = 0, \quad \cdot \quad \cdot \quad \cdot \quad (16)$$

which, integrated, is

$$r \log\left(\frac{Bq+A}{Br}\right) - \log(Bkq^r + A) + \log p = \text{const.}, \cdot (17)$$

and by introducing the boundary conditions, we obtain

$$\frac{B^r q^r \pi_A + A^r \pi_B}{(Bq+A)^r} = p, \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (18)$$

with

$$k = \left(\frac{B}{A}\right)^{r-1} \frac{\pi_A}{\pi_B}. \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (19)$$

But as

$$s = \frac{B}{A} kq^r = \frac{B^r q^r \pi_A}{A^r \pi_B},$$

we have, as in the preceding case, the partial pressures represented by the two terms of the equation; or

$$p_A = \left(\frac{Bq}{Bq+A}\right)^r \pi_A, \quad p_B = \left(\frac{A}{Bq+A}\right)^r \pi_B. \quad \cdot \quad \cdot \quad (20)$$

With regard to equation (18) it is to be noted: 1st, that (14) is a particular case of it, with $r = 1$; 2nd, that when $r = 0$ the pressure of the mixed vapour is the sum of the pressures of the two pure substances; that is the case when the two liquids do not mix; 3rd, that when r has any other (positive) value the function has a maximum or minimum. To find this we must put $\partial p / \partial q = 0$, or (considering the numerator of the differential coefficient only)

$$B^r \pi_A r q^{r-1}(Bq+A)^r - (B^r \pi_A q^r + A^r \pi_B) r (Bq+A)^{r-1} B = 0,$$

whence

$$q = \frac{A}{B}\left(\frac{\pi_B}{\pi_A}\right)^{\frac{1}{r-1}} = \frac{A}{B}\left(\frac{\pi_A}{\pi_B}\right)^{\frac{1}{1-r}}, \quad \cdot \quad \cdot \quad \cdot \quad (21)$$

and the value of

$$p = \frac{\pi_A \pi_B}{\left(\pi_A^{\frac{1}{r-1}} + \pi_B^{\frac{1}{r-1}}\right)^{r-1}} = \left(\pi_A^{\frac{1}{1-r}} + \pi_B^{\frac{1}{1-r}}\right)^{1-r} . \quad .(22)$$

This is a maximum if $r < 1$, a minimum if $r > 1$.

Now cases exist in which p has a maximum (propyl alcohol and water) or minimum (formic acid and water); but in others neither has been observed (methyl or ethyl alcohol and water). If, however, r has any value not very different from unity $\frac{1}{1-r}$ will be large; and the stationary value of p will be for a liquid containing only a very little either of the substance A or B—so little that it would not have been observed in Wüllner's or Konowalow's experiments. The function expressing p cannot have both a maximum and a minimum, and no liquid mixture has been observed to possess both.

4th, at the maximum or minimum point,

$$t = kq^r = \left(\frac{B}{A}\right)^{r-1} \frac{\pi_A}{\pi_B} \times \left(\frac{A}{B}\right)^r \left(\frac{\pi_A}{\pi_B}\right)^{\frac{r}{1-r}} = \frac{A}{B}\left(\frac{\pi_A}{\pi_B}\right)^{\frac{1}{1-r}} = q;$$

i. e. the liquid and vapour have the same percentage composition. That this is necessarily the case when p has a stationary value was first pointed out by Konowalow.

(iv.) *Comparison of the Integral Equation with Experiment.*

The experiments of Wüllner, Konowalow, and F. D. Brown, mentioned above, do not afford much material for testing the accuracy of equation (18). The equation contains one unknown constant, r, so that one observation of the vapour-pressure of a mixture, or of the composition of the vapour rising from it, will enable us to determine r, and if there is more than one mixture so investigated, we have a test of the applicability of the equation. Wüllner observed the pressures of four mixtures of water and alcohol, three of alcohol and ether, and quotes from Regnault three of carbon disulphide and ether. The observations were extended over a range of temperature; but as nothing in our investigation indicates that the quantity r is independent of temperature we get no direct help from this multiplication of data. It will be seen in the sequel, however, that so far as the equation is applicable at one temperature, it is usually applicable with the same value of r at others.

Konowalow gives his observations on the vapour-pressures of the eight liquids he employed, mixed with water, for

several mixtures of different composition in each case. But the results, as well as those of Wüllner on alcohol and water, are not expressible by equation (18) ; that equation is represented by a simply-shaped curve, not possessing the most characteristic features of some of Konowalow's curves—notably those of propyl alcohol and of formic acid.

Brown, as previously mentioned, gives both vapour-pressure and composition of vapour ; the two quantities should, of course, give the same value of *r*. He used, however, only one mixture at any particular temperature—viz., that whose vapour-pressure was 760 millim. Moreover, he states that the vapour was cooled in the upper part of his distilling-flask, so that the vapour which came over was presumably in equilibrium with a liquid of somewhat lower boiling-point (and therefore containing less benzene) than that in the flask.

It will be seen from the form of the equations, that when *t* is given *r* can at once be found. For

$$t=\left(\frac{B}{A}\right)^{r-1} q^r \left(\frac{\pi_A}{\pi_B}\right),$$

or

$$s=\left(\frac{Bq}{A}\right)^r \frac{\pi_A}{\pi_B},$$

giving

$$r=\frac{\log s-\log \dfrac{\pi_A}{\pi_B}}{\log \dfrac{Bq}{A}} \quad . \quad . \quad . \quad . \quad . \quad (23)$$

But when only *p* is given equation (18) must be used, and this cannot be solved directly. It is, however, fairly amenable to logarithmic computation, so that by assuming values of *r* and making successive approximations, the true value may be found without much trouble. An actual example will best show how the approximation proceeds :—

Benzene and Carbon Disulphide at 50° (F. D. Brown).

A (Benzene) = 78.	π_A = 269 millim.
B = 76.	π_B = 857 ,,
With *q* = $\frac{1}{3}$,	*p* (obs.) = 760.
With *r* = 1	*p* (calc.) = 712·8,
·9	742·8,
·87	751·7,
·845	759·3.

The agreement to be looked for between observed and calculated vapour-pressures is not of a high order : Wüllner

in his paper (*loc. cit.*) tabulates the values of $p/(\pi_A + \pi_B)$ for different temperatures; and this quantity, whose constancy or regular changes it was his object to observe, shows irregular fluctuations amounting to one per cent. That may therefore be taken as the order of accuracy of the observations of pressure.

The results obtained are given in the following tables:—

[Explanation of tables:—A, B, molecular weights of the pure liquids; π_A, π_B, vapour-pressures of pure liquids; q, ratio of mass of A to mass of B in liquid; p, vapour-pressure of the mixture; r, constant of equation (18)].

Alcohol and Ether (Wüllner).

A (Alcohol) = 46 ;   B = 74.

Temp. 7°·2. $\pi_A = 24\cdot37$. $\pi_B = 264\cdot7$. $r = \cdot5$.

q.	p (calc.).	p (obs.).
1	183·0	183·0
·5	213·3	215·0
·25	236·6	231·6

Temp. 16·2. $\pi_A = 38\cdot25$. $\pi_B = 379\cdot2$. $r = \cdot5$.

q.	p (calc.).	p (obs.).
1	265·9	261·6
·5	307·8	305·0
·25	340·7	329·9

Temp. 25·5. $\pi_A = 66\cdot25$. $\pi_B = 553\cdot0$. $r = \cdot5$.

q.	p (calc.).	p (obs.).
1	394·4	392·7
·5	455·9	448·2
·25	502·4	478·0

The formula indicates that with $q = \cdot005$ nearly, p is a maximum and equal to 265·8 millim., or ·9 millim. more than the saturation pressure of pure ether.

Carbon Disulphide and Ether (Regnault).

A (Carbon Disulphide) = 76 ;   B = 74.

Temp. 9°. $\pi_A = 190\cdot75$. $\pi_B = 274\cdot85$. $r = \cdot79$.

q.	p (calc.).	p (obs.).	
1	268·7	272·7	(equal weights)
1·385	264·6	263·8	(44 per cent. of CS_2 by volume)
2·936	245·1	249·1	(62 per cent. of CS_2 by volume)

Temp. 20°. $\pi_A = 301\cdot78$. $\pi_B = 433\cdot26$. $r = \cdot79$.

q.	p (calc.).	p (obs.).
1	425·9	no obs.
1·385	417·8	414
2·936	387·2	387

Temp. 30°. $\pi_A = 436\cdot97$. $\pi_B = 636\cdot33$. $r = \cdot79$.

q.	p (calc.).	p (obs.).
1	621·9	no obs.
1·385	609·7	602
2·936	563·7	560·9

These are the only measurements of vapour-pressures, that I have been able to find, sufficiently extensive to serve as a test for the theory given above. In addition, there are the measurements of F. D. Brown on the composition of the distillate from a mixture of benzene and carbon disulphide ; these were carried out by the ordinary method of fractionation at constant (atmospheric) pressure, and therefore at a temperature varying from 47°·8 to 76°·9. To make use of them, a diagram was drawn showing the relation between log q (ratio of masses in liquid) and log t (ratio in vapour) This was found to show a slight curvature, convex to the axis of q, in accordance with the fact that the ratio of the vapour-pressures of the pure substances (π_B/π_A) decreases as the temperature rises. The set of observations, however, could be represented with fair approximation by the straight line

$$\log t = \overline{1}\cdot48 + 0\cdot9 \log q.$$

from this are derived the numbers in the third column below. The table gives the reduced results of Brown's observations, unlike those quoted from Wüllner and Regnault, which give direct experimental numbers.

Per cent. benzene in liquid.	Do. in vapour (obs.).	Do. in vapour (calc.).	Log π_B/π_A.	Temperature.
95	82·0	81·0	·4396	76·2
90	69·4	68·1	·4474	72·5
85	59·3	59·0	·4539	69·4
80	51·3	51·3	·4591	66·6
70	38·8	39·3	·4700	62·2
60	29·3	30·3	·4779	58·8
50	22·3	23·2	·4853	55·7
40	17·1	17·3	·4920	53·0
30	12·3	12·3	·4972	50·9
20	8·2	8·0	·5016	49·2
10	4·1	4·1	·5053	47·8

Now from equation (19) we have

$$\log \pi_B/\pi_A = (1-r) \log \frac{A}{B} - \log k.$$

Introducing the numbers for benzene and carbon disulphide, we find

$$\log \pi_B/\pi_A = \cdot 5211.$$

(v.) *New Experiments.*

In order to test the theory developed in the foregoing sections, and especially the accuracy of the expression adopted for the relation of the composition of the vapour to that of the liquid, experiments were undertaken. The mixtures chosen were of benzene with ethyl acetate and benzene with methyl acetate, as those three liquids can be obtained with ease in a reasonably pure state, and their physical properties —such as vapour-pressure and vapour-density—show no abnormalities. The constituents of the first pair have nearly the same vapour-pressure, so that their mixture is well adapted to show the phenomena attending the existence of the maximum of the curve connecting vapour-pressure with composition : while benzene and methyl acetate, on the other hand, have widely different boiling-points, and a corresponding wide difference between the composition of the liquid mixture and its vapour.

The method adopted for measuring the relation between the compositions (relation between q and t) was one of distillation. The apparatus, which presented no very noteworthy features, consisted of (a) a distillation-flask of about 100 cub. centim., its neck closed by a rubber stopper, through which a thermometer passed ; this was heated in a large water-bath ; (b) a smaller distillation-flask with its neck fitted over the side-tube of (a) ; its bulb was immersed in a mixture of ice and salt ; (c) a water-pump leading through a gauge and large air-chamber to the side-tube of (b).

In carrying out an experiment, the bath was heated to about 52° or 53°, and kept at that by a thermostat (of Ostwald's usual type) attached to it, so that the liquid in the flask might distil over slowly as near to 50° as possible. The pressure in the air-chamber (but not in the flask and receiver) was then reduced sufficiently; its connexion with the pump closed by a screw pinchcock, and that with the flask and receiver opened. In this way the pressure on the liquid was reduced at once to the amount required, and all the distillate came over at practically the same temperature. On reducing

the pressure in this way the liquid boiled gently, and in a minute or two enough had collected in the receiver to be withdrawn for analysis, *i. e.* about 2 cub. centim. The operation was repeated three or four times on the same mixture, without removing it from the flask, and analyses made of the distilland before and after the whole experiment.

The method of analysis that enabled me to use such small quantities of liquid, and at the same time to work very expeditiously, consisted in determining the refractive index by a Pulfrich refractometer. This instrument—of the usual type —was of sensitiveness enough to give the refractive index to about ·00005 (corresponding to about half a minute in the angle reading). Now, for benzene $\mu = 1·50$, while for the two esters it is about 1·37 ; hence a change of composition of $\frac{1}{10}$ per cent. would cause a change in the refractive index of ·00013, and could quite well be detected. To attain that degree of accuracy it was necessary to know the temperature to about $\frac{1}{10}$ degree ; as the temperature-coefficient is ·00052 to ·00065 per degree. The measurements were carried out in a room that rarely differed by one degree from 18°, and it was therefore thought sufficient to interpolate the temperature coefficients of the mixtures from those of the pure substances given in Landolt and Börnstein's tables, and reduce all the observations to that temperature.

The preliminary measurements of the refractive index of the mixtures weighed out for the purpose, gave the following results :—

Benzene and Ethyl Acetate.

Per cent. of benzene by weight.	Temp. of experiment.	μ (obs.) reduced to 18°.	μ (additive).	μ (calc.).	$\mu_{calc.} - \mu_{obs.}$
0	17·6°	1·37326			
13·88	16·1	1·39095	1·39117	1·39069	− ·00026
27·92	16·0	1·40870	1·40931	1·40850	− 20
44·67	16·0	1·42991	1·43093	1·42994	+ 3
55·85	15·4	1·44424	1·44537	1·44438	+ 14
69·40	16·4	1·46219	1·46287	1·46203	− 16
86·76	16·4	1·48501	1·48529	1·48482	− 19
100	17·8	1·50238			

The fourth column gives the values of μ calculated on the supposition that it is a strictly additive property, *i. e.*,

$$= 1·37326 \, (1-x) + 1·50238 \, x,$$

where x is the fractional amount of benzene present. The

differences between that value and the observed were plotted, and a parabolic curve drawn to represent them ; in this way I arrived at the following equation for the refractive index :

$$\mu_{(calc.)} = 1{\cdot}37326\,(1-x) + 1{\cdot}50238\,x - {\cdot}00100 + 00400\,(\tfrac{1}{2}-x)^2.$$

from which the numbers in the fifth column above are derived.

A table showing the relation between composition and refractive index was then prepared, and by reference to it the composition of any mixture examined with the refractometer could at once be determined.

In the same way for

Benzene and Methyl Acetate.

Per cent. benzene.	Temp.	μ (obs.). reduced to 18°.	μ (additive).	μ (calc.).	$\mu_{calc.} - \mu_{obs.}$
0	19·4	1·36283			
0	17·2	1·36293			
	(mean	1·36288)			
9·38	17·0	1·37575	1·37596	1·37569	− ·00006
16·88	17·5	1·38586	1·38642	1·38597	+ ·00011
32·46	17·6	1·40769*	1·40816	1·40746	− ·00023
45·16	17·2	1·42511	1·42588	1·42509	− ·00002
63·76	17·2	1·45100	1·45183	1·45109	+ ·00009
75·45	17·2	1·46739	1·46813	1·46754	+ ·00015
93·74	16·8	1·49356	1·49357	1·49339	− ·00017
100	18·8	1·50246			
100	16·8	1·50231			
	(mean	1·50238)			

* Observation doubtful.

The numbers in the fifth column are derived from the equation

$$\mu = 1{\cdot}36288\,(1-x) + 1{\cdot}50238\,x - {\cdot}00080 + {\cdot}00320\,(\tfrac{1}{2}-x)^2.$$

After these preliminary experiments, a number of mixtures were distilled as described above ; the liquid in the flask, sampled before and after, showed no appreciable change in the case of the ethyl mixtures, and in that of the methyl rarely more than 1 per cent. The mean value was therefore taken as giving q the composition of the distilland. Of the distillate three samples were usually taken ; the first occasionally contained a slightly lower percentage of benzene, owing to the greater condensation of that liquid—the less volatile—on the delivery tube ; the others usually agreed to within one or two tenths per cent. The results are given in the following tables :—

Benzene and Ethyl Acetate.

Per cent. benzene in liquid.	Do. in distillate.	Temp. of distillation.	q.	t.	t (calc.).	Per cent. in distillate (calc.).
12·9	13·05	50·3	·1481	·1501	·1514	13·15
25·85	25·7	50·5	·3486	·3459	·3449	25·65
50·9	49·7	49·3	1·037	·9881	·9845	49·6
51·0	49·8	50·2	1·041	·9920	·9881	49·7
75·6	73·9	48·7	3·098	2·831	2·822	73·8
87·45	85·85	52·0	6·968	6·067	6·153	86·0

It should be noted that the first of the above mixtures gives a distillate containing more benzene than itself; thus showing that its saturation-pressure must be greater than that of pure ethyl acetate; and that there must be some mixture (containing more than 12·9 per cent. of benzene) having a maximum vapour-pressure, and distilling without change of composition.

A diagram was drawn showing the relation between $\log q$ and $\log t$. This was found to be practically linear, in accordance with the assumption made in the earlier sections that $t = kq^r$, and could best be represented with the constants $\log k = \overline{1}\cdot978$, $r = 0\cdot962$. From this are derived the numbers in columns 6 and 7 above; the agreement with the observed percentages is within the limit of errors of observation.

Benzene and Methyl Acetate.

Per cent. of benzene in liquid.	Do. in distillate.	Temp. of distillation.	q.	t.	t (calc.).	Per cent. in distillate (calc.).
18·5	11·8	50·0	·2276	·1335	·1299	11·5
31·0	19·4	48·5	·4495	·2407	·2429	19·55
47·95	32·1	50·0	·9208	·4730	·4700	32·0
67·0	49·1	49·6	2·032	·9638	·9734	49·3
86·0	73·45	51·0	6·153	2·769	2·698	72·95

The numbers in the last two columns are calculated from the equation

$$\log t = \overline{1}\cdot705 + 0\cdot92 \log q.$$

The temperature of distillation was not as constant as is desirable; but in view of the results of Brown's experiments discussed in the preceding section, it is not likely that any considerable error has arisen on that account.

In the same way as in the preceding section, we may calculate the value of π_B/π_A. For benzene and ethyl acetate we have

$$\log \pi_B/\pi_A = \cdot038 \times \log \frac{78}{88} - \bar{1}\cdot978 = \cdot020.$$

To compare with this we have as the vapour-pressure of benzene at 50° according to S. Young 269 millim., or Regnault 271 millim.; while from O. Schumann's observations (Wied. *Ann.* xii. p. 47) that of ethyl acetate is 284 millim. Now $\log \dfrac{284}{269} = \cdot0235$, $\log \dfrac{284}{271} = \cdot0203$.

Similarly for benzene and methyl acetate

$$\log \pi_B/\pi_A = \cdot08 \log \frac{78}{74} - \bar{1}\cdot705 = \cdot297,$$

and Schumann's experiments give π_B (for methyl acetate) $= 588$ millim.

$$\text{Log } \frac{588}{269} = \cdot3396, \text{ and } \log \frac{588}{271} = \cdot3364.$$

The discrepancy in this case is more serious than in the other two.

For the further testing of the theory, some preliminary experiments on the vapour-pressure of mixtures of the liquids used have been carried out. They, together with the results detailed above, seem to indicate that while the theory of the present memoir may serve as a useful introduction to this almost untouched subject, it will require emendation before representing the facts with the degree of accuracy attainable in the experiments themselves. Probably the weakest point of the theory lies in the assumption that the vapours obey Boyle's law up to the moment of condensation, and better agreement may be looked for when allowance is made for the greater density of the nearly saturated vapour, in calculating the thermodynamic potential. I hope to be able to continue the research along the lines here indicated, both of theory and experiment.

The experimental part of this research was carried out in the laboratory of Prof. Ostwald, at Leipzig, and it gives me much pleasure to express my thanks to him and to Dr. Le Blanc for the many valuable suggestions as to methods, and other assistance for which I am indebted to them.

XXXVI. *An Improved Calorimeter for the Application of the Method of Mixtures.   By* F. A. WATERMAN[*].

THE determination of the specific heat of solids by the Method of Mixtures, as employed by Regnault, is especially subject to error arising from the determination of the radiation correction.   For the purpose of avoiding this source of error, Mr. M. N. Hesehus[†] has suggested that the calorimeter-cup be introduced into the bulb of an air-thermometer and maintained at a constant temperature by the introduction of a sufficient amount of cold water, of known temperature, immediately after the introduction of the heated solid.   By this means both the radiation-correction and the "water equivalent" of the calorimeter-cup are avoided.

The heat received by the cold water being equal to that given out by the heated body, the following simple equations may be used :—

$$MS(T-\theta) = ms(\theta-t),$$

in which

M = mass of substance, the specific heat of which is to be determined.

m = mass of cold water introduced into the calorimeter-cup.

T = temperature of the heated body.

θ = initial temperature of the calorimeter-cup.

t = temperature of cold water introduced into calorimeter-cup.

s = mean specific heat of water at the temperature used.

S = specific heat sought.

From this equation we have

$$S = \frac{ms(\theta-t)}{M(T-\theta)},$$

the working equation used.

The results obtained by this method, as submitted by Mr. Hesehus, do not appear to be as accurate, however, as those obtained by the Method of Mixtures as practised by Regnault.   The ten determinations given of the specific heat of brass varied from ·0821 to ·0969, or, omitting the result ·0821, which was apparently erroneous, nine determinations

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varied from ·0908 to ·0969, the probable error of the mean of the whole being much higher than is usual in the case of a similar series of results obtained by Regnault's method.   As the above method appeared to be a desirable one for some work in hand, I have endeavoured to perfect a calorimeter by means of which it might be applied with greater accuracy.

The form of apparatus which I have devised has proved very satisfactory after repeated trials, as is shown by the results here submitted.   It consists essentially of the following parts (see figure) :—
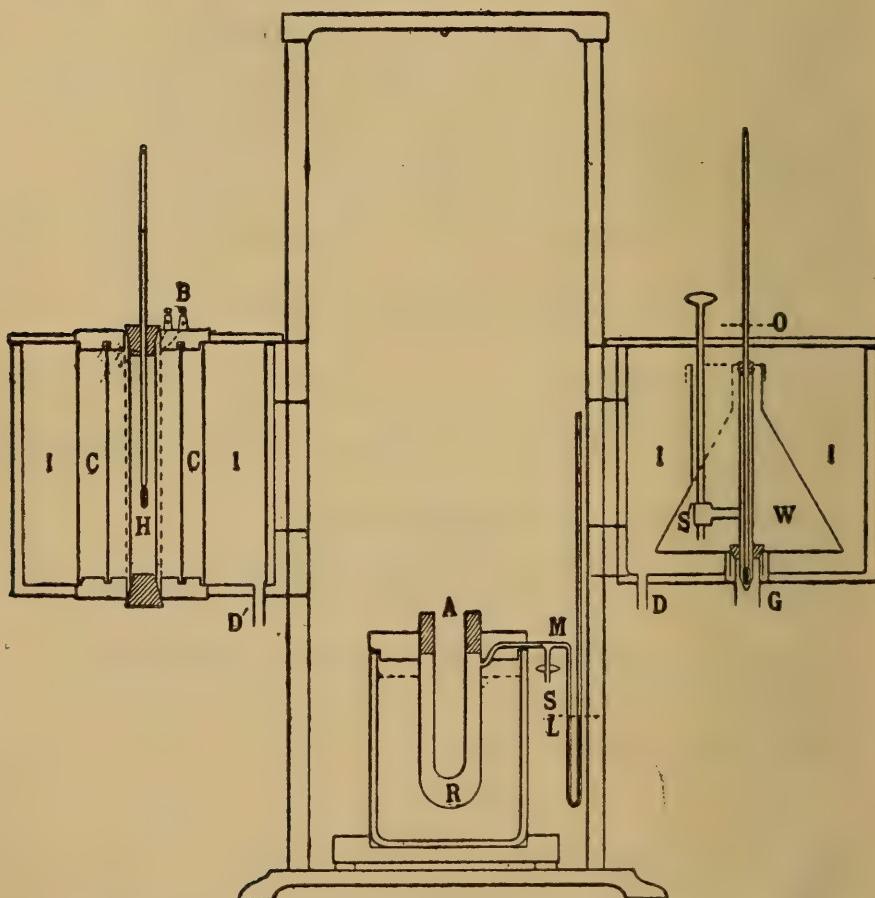
A glass jar which supports, by a wooden cover, the bulb R of a glass air-thermometer, the manometric tube M of which, in the form of a capillary U-tube, is supported in a vertical position.   The manometric tube is supplied with a stopcock S.   The glass jar is kept nearly full of water for the purpose of maintaining the thermometer-bulb constantly at room-temperature and preventing any sudden variation of temperature due to air-currents.   For the purpose of increasing the sensitiveness of the thermometer, the liquid selected was

one of low density, and kerosene, of specific gravity approximately $\frac{8}{10}$, was taken. The air-thermometer thus constructed proved very sensitive, and a change in the temperature of the calorimeter-cup of $\frac{1}{100}°$ C. was clearly shown by an elevation of the manometric column.

The calorimeter-cup A is made in the form of a tube of silver, $\frac{1}{10}$ millimetre in thickness, of the general form of a test-tube, cemented to a rubber stopper which may be inserted air-tight into the thermometer-bulb*. Silver was selected as the material used for the cup on account of its high conductivity for heat, which causes the temperature of the cup to quickly become that of its contents. The lower half of the outer surface of the tube is coated with a thin layer of lamp-black mixed with turpentine and shellac, for the purpose of increasing its radiating power.

The water-cooler and dropper is supported upon a vertical rod in such a manner that it may be quickly turned about the rod as an axis, and may deliver water directly to the calorimeter-cup. The cooler consists of a copper receiver covered with heavy felt, within which the water-receiver W is placed. A drainage-tube D, provided with a rubber-tube connexion, conducts away the water from the melting ice I with which the receiver is filled. The water-receiver W is made in the form of an inverted cone of tin-plated copper. This form has been found most satisfactory for maintaining the water at constant temperature, as the ice, resting upon the sides of the receiver, cannot melt away from them, leaving an intervening air-space. The water-dropper consists of a syphon, within the longer arm of which a thermometer is introduced, the bulb of which is held very near the small orifice from which the water drops when the stopcock S′ is opened. Thus no barrier is interposed at any time between the thermometer-bulb and the point of delivery of the cold water. The thermometer used is graduated into tenths of a degree Centigrade scale, and hundredths of a degree may readily be estimated. The zero-point of the scale is just above the cover of the ice-receiver, the stem being immersed in cold water nearly up to that point.

An electric heater is supported upon a second vertical rod, and may be turned about the rod as an axis until the heater H is directly over the calorimeter-cup, allowing the heated body to be transferred directly to the cup. The heater, which

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* This device was first used, but the calorimeter as now made has an air-tight connexion in this part, similar to that used in the calorimeter for the Method of Cooling as usually applied. All errors due to leakage of air at stopper, &c., which might arise at this point, are thus avoided.

is somewhat similar in form to that designed by Prof. Henry Crew [*], consists of a copper tube H, about which is wound a heating-coil of german-silver wire, insulated from the tube by narrow strips of asbestos-paper. This is enclosed within a larger tube, and all is inserted within an ice-receiver I, the space C being packed with cotton to prevent convection-currents. Water from the melting ice of the ice-receiver escapes from the drainage-tube D' by means of a rubber-tube connexion. The temperature of the outer wall remaining constantly that of the melting ice, the fall of temperature remains constant between the inner and outer walls as long as heat is uniformly supplied to the inner chamber. This is readily maintained by a constant electric current supplied to the heating-coil, through the binding-screws B, from a storage-battery of sufficient capacity having a variable resistance in its circuit. The battery which has been used maintained a normal electromotive force of 100 volts. The temperature of the heater is readily maintained constant within $\frac{1}{10}$° C. for five or six hours, at any temperature desired for the conditions of the work in hand, from $\frac{2}{10}$ to $\frac{6}{10}$ amperes of current being required according to the temperature desired. The thermometer, for the determination of the temperature of the heated body, is supported by a cork inserted in the top of the tube H. The bottom of the tube is closed by a cork, which is removed to allow the solid to pass into the calorimeter-cup when heated [†].

The method of making a determination of the specific heat of a metal by means of this calorimeter is as follows:—

The metal may be suspended in the heater in small fragments, contained in a basket of fine wire gauze of known specific heat, as employed by Regnault ; or, if in the form of sheet metal or fine wire, may be suspended in contact with the thermometer-bulb by a thread of known weight. In the case of metal of low melting-point I have cast thin cylinders, slightly smaller in diameter than the calorimeter-cup, which were so suspended in the heater that the bulb of the thermometer was within the cylinder while heating. The thermometer used is graduated into fifths of a degree Centigrade scale, and hundredths of a degree may readily be estimated. The metal is then maintained at the desired temperature from one-half to three-quarters of an hour, according to the conductivity of the metal used.

* Philosophical Magazine, [5] xxxiii. 1892.
† The heater, as now made, has a sliding cover which closes the bottom of the tube while the body is heating, and automatically opens as the heater is turned around into position to deliver the heated body to the calorimeter-cup.

The silver tube, which forms the calorimeter-cup, is then withdrawn from the bulb of the air-thermometer, pure water at room-temperature is introduced in sufficient quantity to cover the metal used, and the whole is carefully weighed. The cup is then placed in position in the bulb of the air-thermometer, the stopcock S being opened while the rubber stopper is pressed firmly into place to insure an air-tight joint. Any " crawling " of the rubber stopper is easily detected by closing the stopcock S, and observing whether the manometric column remains stationary. A few moments are allowed for this observation in each experiment. Any variation in the temperature of the cup is also readily detected in this observation. In each observation the manometric column has been found to remain stationary after a very short time.

The initial temperature of the calorimeter-cup, which remains at room-temperature, is then taken by means of a thermometer suspended within the cup having its bulb in contact with the side of the cup, but not touching the water. This is found to remain practically constant throughout a series of observations, agreeing with the temperature of the water in the jar. The thermometer used is graduated into twentieths of a degree Centigrade scale, and hundredths of a degree may readily be estimated.

Water is allowed to drop from the water-dropper, and its thermometer read as soon as its temperature becomes constant. This occurs after a few drops have fallen. The manometric column is then brought to the same level L in each arm of the U-tube, by opening the stopcock S. A strip of white cardboard attached to the U-tube, with a horizontal ink-line at the back of the level surface of the manometric liquid, renders the position of the liquid column plainly visible. The stopcock is then closed, the heater turned around into position, and the heated metal quickly introduced into the cup. The heater is then turned back and the water-dropper quickly turned into position and water allowed to drop into the cup, at first rapidly, then more slowly until the manometric column remains at its original position, indicating that the initial temperature of the cup has been maintained. For several moments the manometric column is then observed, in order to make sure that the heated body has acquired the exact temperature of the cup. In the case of a body of poor conductivity the cold water is more slowly introduced, as the heat from the body is more slowly transmitted to the water.

The specific heat of substances of poor conductivity may thus be obtained with great exactness ; the mixture being practically at room-temperature, radiation loss is inappreciable during the time spent in observing the manometric column,

and in adding water just sufficient in amount to maintain the initial temperature of the cup.   A little practice in the manipulation of the calorimeter enables the operator to keep the cup practically at its initial temperature throughout each determination, thus obviating the use of radiation correction and " water equivalent " of the cup.   The falling of the cold water from the water-dropper into the tube-shaped cup also serves to agitate the water in the cup, and keeps its temperature uniform without the use of a stirrer.

The cup and its contents are then removed from the bulb of the air-thermometer and weighed.   The weight thus obtained minus the initial weight of the cup, water contained, and weight of metal used, gives the weight of cold water added. The loss in weight due to the evaporation of the water in the cup, during the time required for the necessary observations, is practically inappreciable, as the average loss was found to be less than $\frac{3}{10}$ milligramme.   If desired, a correction based upon preliminary observations may be introduced to compensate for this loss.

The necessary operations, briefly stated, are thus :—

The heating and the determination of the temperature of a body of known weight.

Weighing of the cup containing a suitable amount of water.

Determination of the initial temperature of the cup.

Introduction of the heated body into the cup, quickly followed by the introduction of an amount of cold water sufficient to maintain the initial temperature of the cup ; the temperature of the cold water being observed during this operation.

Final weight of the cup and its contents determined, and the weight of cold water added determined from data obtained.

Calculation of result by use of the equation

$$S = \frac{ms(\theta - t)}{M(T - \theta)}.$$

The results obtained by the use of this calorimeter, which are here given, are but a summary of some trial determinations made from time to time as the apparatus was being improved *.   As chemically pure metals were not at hand, the results obtained are submitted simply for the illustration

of the accuracy with which determinations may be made, and are not considered to be exact values of the specific heats of pure metals.   It is hoped that the results, for the determination of which the calorimeter was designed, may be presented at an early date.   In the calculation of results, s, the specific heat of the water used, was taken as unity.   The three thermometers used for the heater, cup, and water-cooler were made by Mr. H. J. Green, of Brooklyn, N.Y., and were standardized by comparison with Yale Observatory Standard No. 59, made by Tonnelot of Paris, and standardized at the Yale College Observatory by Prof. Leonard Waldo.   All weighings were made upon a balance sensitive to $\frac{1}{10}$ milligramme under the given load.

Cadmium.—As supplied for chemical use, purity unknown.
Cast in the form of a thin cylinder.

1895.	M.	t.	θ.	T.	m.	S.
Jan. 26	13·2481	·30	11·12	85·60	5·0425	·05529
Feb. 23	,,	2·51	15·00	93·38	4·601	·05534
May 18	,,	·42	24·15	100·10	2·3675	·05583

No mean taken on account of different temperatures used.

Copper.—99·98 % pure ; from Lake Superior.   Two pieces taken from a thin bar of drawn metal.

	M.	t.	θ.	T.	m.	S.
July 1	10·9322	·19	23·39	100·0	3·4204	·09475
,, 2	,,	·30	22·42	100·2	3·6403	·09470
,, 1	23·6625	·25	23·62	99·8	7·302	·09467
,, 2	,,	·30	21·51	100·0	8·296	·09474
				Mean		·09471

Glass.—Composition unknown.   Two pieces taken from a piece of thin-walled tubing.

	M.	t.	θ.	T.	m.	S.
July 3	7·501	·33	23·75	99·95	3·5165	·14409
,, 5	,,	·12	21·32	99·90	4·0043	·14402
,, 5	7·3571	·10	20·84	100·00	4·0549	·14439
				Mean		·14417

Gold.—Nearly pure.   In the form of a thin bar.

	M.	t.	θ.	T.	m.	S.
July 3.........	17·8292	·20	24·00	100·00	1·7456	·03066
„ 3.........	„	·25	24·41	100·00	1·7101	·03065
„ 5.........	„	·35	23·45	99·95	1·8153	·03074
				Mean		·03068

Zinc.—As supplied for chemical use, purity unknown.
In the form of a thin cast bar.

	M.	t.	θ.	T.	m.	S.
Mar. 15	20·3805	·20	23·40	99·9	6·416	·09547
„ 15	„	·20	23·50	100·0	6·386	·09544
„ 16	„	·27	23·85	100·2	6·3017	·09549
				Mean		·09547

Alloy.—Melting-point 70° C.   Bismuth 4 parts, Cadmium 1 part, Lead 2 parts, Tin 1 part.   Metals used were supplied for chemical use ; purity unknown.

	M.	t.	θ.	T.	m.	S.
Feb. 15.........	16·108	2·53	21·94	60·66	1·1475	·03571
„ 15.........	„	3·12	21·76	60·42	1·1913	·03566
„ 16.........	„	1·60	21·66	59·67	1·0875	·03563
„ 18.........	„	2·51	21·93	59·45	1·1080	·03560
„ 19.........	„	2·93	21·08	60·26	1·2390	·03563
				Mean		·03565

This method may readily be extended over a considerable range of calometric work. The electric heater permits the heating of the body under investigation to any temperature ordinarily desired. The body may be cooled by a suitable freezing mixture, and the initial temperature of the cup maintained by the introduction of warm water of known temperature, thus extending the range of temperatures throughout which an investigation may be carried. The specific heat of a liquid may be determined by enclosing it in a suitable vessel, the constants of which have previously been determined. Some liquid other than water may be found preferable for special work, and may readily be used in the cup and cooler. Aniline, the use of which is advocated by Mr. E. H. Griffiths*, has a smaller capacity for heat and a higher boiling-point

* Philosophical Magazine, xxxix. p. 47, 1895.

than water. It would, therefore, increase both the sensitiveness of the calorimeter in measuring small quantities of heat and the range of temperatures throughout which an investigation might be carried.

This calorimeter, as now made, enables the experimenter of ordinary skill in manipulation to obtain results which are comparable in accuracy and consistency with those obtained by any calorimetric method in use ; ordinary care in weighing and in reading the thermometers used being the most important considerations to be observed. For these reasons it is well calculated for student use as well as for research-work, for which its wide range of application makes it especially suitable.

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            Princeton, N.J., U.S.A.

XXXVII. *The Viscosity of Mixed Gases.*
By WILLIAM SUTHERLAND[*].

NEARLY fifty years ago Graham, in his beautiful experiments on the motion of gases, encountered the fact that by mixing a little hydrogen with carbonic dioxide the mixture can be rendered more viscous than the carbonic dioxide, although the hydrogen is less viscous than it. The fact seems to have arrested his attention rather strongly ; for he made a large number of experiments on the transpiration of mixed gases through capillary tubes, with the result that, if t_1 is the time of transpiration of a gas 1 under certain conditions as to pressure and temperature, and t_2 the time for a gas 2 under the same conditions, then for a mixture of n_1 volumes of 1 with n_2 volumes of 2 the time t is in most cases given with considerable accuracy by the empirical formula

$$(n_1 + n_2)\, t = n_1 t_1 + n_2 t_2\ ;$$

but when hydrogen is one of the ingredients, the formula fails entirely to represent facts. As the viscosity is proportional to the time of transpiration, a similar empirical formula holds for the viscosity of most mixtures, but fails for those containing hydrogen. This peculiar experimental fact also arrested Maxwell's attention ; for in his Bakerian lecture in 1866, on the viscosity of gases, he mentions it as a remarkable thing that while hydrogen is only half as viscous as air, a mixture of equal volumes of hydrogen and air is 15/16 as viscous as air. Maxwell's measurements of viscosity were made with

his oscillating-disk apparatus, and were therefore specially suitable for controlling Graham's results. But in 1879 Puluj went into the subject more thoroughly by carrying out with an oscillating-disk apparatus a large number of measurements of the viscosity of mixtures of carbonic dioxide and hydrogen, which had proved to be the most exceptional of all with Graham : his results were completely confirmatory of Graham's.

But to my knowledge the theory of this interesting phenomenon has not hitherto been undertaken, though apparently so suited to serve as a test-case for the kinetic theory. Doubtless the general principles of the kinetic theory are now so well established as to hardly require further confirmation ; but still, apart from the interest in the problem for its own sake, it will be advantageous to consider the theory of it, because in pushing on with investigations of the properties of molecules it is very desirable at the present juncture to ascertain how far the simplest hypotheses will carry us and where they cease to be sufficient. Moreover an inquiry into the theory of the viscosity of mixed gases offers an additional advantage in throwing light on the theory of the viscosity of a single gas.

In the theory of the viscosity of a gas we suppose the gas to be confined between two parallel solid planes, one of which is at rest and the other moving in a fixed direction in its own plane with velocity w. It has been proved experimentally that the slipping which takes place at either solid plane can be neglected, unless the distance between the planes is only a small multiple of the mean free path of the molecules of the gas. Neglecting the slipping then, and denoting the distance between the planes by D, the velocity of the gas in a layer at distance x from the fixed plane is wx/D, and on the average each molecule in the layer has this velocity in addition to its velocity of agitation. The viscous action between the two parts of the gas on opposite sides of the parallel plane at distance x from the fixed one, is due to the velocities of agitation carrying velocities greater than wx/D from distances greater than x to distances less than x, and *vice versâ*. To follow the conversion of the molar energy due to the velocities wx/D into molecular energy, that is, to follow the conversion of the molar energy into heat by the action of the gaseous friction, we have to consider the collisions taking place in the layer at x between molecules coming from its opposite sides, and these may be said to come on the average from distances $x+l$ and $x-l$: consequently the velocity of the centre of gravity of each colliding pair both before and after collision is wx/D, which is the permanent velocity characteristic of the

layer at x. Of course the average effect of the collision is largely to destroy the two small relative velocities lx/D and $-lx/D$, and to convert the energy associated with them into energy of agitation. This is easily proved in the theory of viscosity, and then it is assumed that on the average a single collision suffices to bring a pair of colliding molecules both into the permanent state characteristic of the layer in which they collide. But, as will be shown below, a single collision does not on the average suffice to bring about this state ; and the difficulty of defining in a simple manner the state of the molecules in any layer at any instant, makes the relation between viscosity and the constants of the molecules not so definitely specifiable as in the numerical relations hitherto given. What appears to me a better statement of the motions of the molecules in each layer will be given below, though the matter is really of slight importance in the case of a single gas; but when it comes to a question of a mixed gas, then a correct specification of the state of each layer becomes the essence of the problem.

In the theory of the viscosity of a single gas, then, it is customary to regard only those molecules which collide in a layer as being characteristic of that layer, those molecules which are passing through it without collision being taken account of in some other layer where they do collide. An approximate expression for the viscosity of a single gas can be very easily established; for if λ is the mean free path, then, as the mean paths have their directions evenly distributed in space, the mean projection of the free paths on the axis of x is the mean distance of a hemispherical surface of radius λ from the diametral plane, which is $\lambda/2$. Thus all the molecules which cross our plane at x may be said on the average to have experienced their last encounter at distances $\lambda/2$ and $-\lambda/2$ from it, so that each molecule that crosses from a distance greater than x carries on the average momentum of amount $mw\lambda/2D$. If there are n molecules in unit volume with average velocity v, then in unit time $nv/6$ may be taken as the number of molecules crossing unit area ; so that the positive momentum carried in unit time across unit area in our plane from distances greater than x is $nvmw\lambda/12\,D$, and the same amount of negative momentum is carried in the opposite direction across unit area, so that the total effect is $nmvw\lambda/6D$, in which $nmv\lambda/6$ is the viscosity η.

The constant $1/6$ is not exact because of the rough and ready approximations ; but, for the purpose in hand, it may be regarded as not very different from the more accurate $\cdot064$, which takes its place as the result of the elaborate

solution (see, for instance, Tait, Trans. Roy. Soc. Edinb. xxxiii. and xxxv.). But the exact value of the constant does not concern us in our present problem, which is to determine the viscosity of a mixture of gases in terms of the viscosities of the pure gases and not absolutely. Accordingly we can avail ourselves of the above easy and convenient method of evaluating the viscosity of a mixture. With v the mean velocity of the molecules of the single gas, and ν the average number of collisions experienced by a molecule in a second, then $\lambda = v/\nu$, and our result for a single gas becomes

$$\eta = nmv^2/6\nu. \quad \ldots \ldots \ldots \quad (1)$$

Now according to the kinetic theory for forceless, smooth, perfectly restitutional, spherical molecules of radius a, and mean square velocity $3\kappa^2/2$ (see, for instance, Tait, Trans. Roy. Soc. Edinb. xxxiii.),

$$\nu = 2n(a+a)^2 \pi^{\frac{1}{2}}(\kappa^2 + \kappa^2)^{\frac{1}{2}} ; \quad \ldots \ldots \quad (2)$$

and by these two equations the viscosity is expressed solely in terms of the given mechanical constants of the system of molecules.

In the case of a mixture of two gases, 1 and 2, let the proportions be n_1 molecules of 1 to n_2 molecules of 2 in unit volume ; then the number of encounters that a molecule of 1 experiences in unit time with molecules 2 may be denoted by $_1\nu_2$, and

$$_1\nu_2 = 2n_2(a_1+a_2)^2 \pi^{\frac{1}{2}}(\kappa_1^2 + \kappa_2^2)^{\frac{1}{2}}; \quad \ldots \ldots \quad (3)$$

(see Tait, Trans. Roy. Soc. Edinb. xxxiii.) ; and the number of encounters per second of a molecule of 1 with other molecules of 1 is

$$_1\nu_1 = 2n_1(a_1+a_1)^2 \pi^{\frac{1}{2}}(\kappa_1^2 + \kappa_1^2)^{\frac{1}{2}}. \quad \ldots \ldots \quad (4)$$

Then v_1 being the average velocity of a molecule of 1, its mean free path in the mixture is

$$\lambda_1 = v_1/(_1\nu_1 + _1\nu_2). \quad \ldots \ldots \ldots \quad (5)$$

Then if, as in the case of a single gas, we assume that a single collision even between molecules of 1 and 2 suffices on the average to bring them to the characteristic state of the layer in which they collide, we can take the viscous action due to the molecules of 1 as given by the above simple theory of a single gas, namely $n_1 m_1 v_1^2 w/6(_1\nu_1 + _1\nu_2)$ D. But of course this assumption is quite unjustifiable, except in the case where the molecule of 1 has the same mass as that of 2, in which case it becomes just as allowable as in that of a single gas, neither more nor less. When m_1 is different from m_2, then if the two solid planes and the mixed gas between them were at

rest, the effect of collisions between the two sets of molecules would be to keep $m_1\kappa_1^2 = m_2\kappa_2^2$. If one of the solid planes is set in motion with velocity w, then on the average a molecule of 1 and a molecule of 2 coming from opposite sides of the layer at x to collide in it will, in addition to the velocities of agitation, have velocities $(x + \lambda_1/2)w/D$ and $(x - \lambda_2/2)w/D$. And the velocity of the centre of mass of the two molecules is not wx/D, characteristic of the layer at x; so that to assume that a single collision between a 1 and a 2 suffices to bring both to the state characteristic of the place where the collision occurs is much less justifiable than in the case where 1 and 2 are identical. It is true that, corresponding to the pair we have just considered, there is another pair whose relative positions are the reverse, so that the velocity of the centre of mass of the four molecules both before and after their collisions is the wx/D characteristic of the layer where they collide; but it is quite evident that there must be further collisions before the four molecules can be treated as typical.

It simplifies the course of the work if for the moment we ignore this difficulty and push on for an expression for the viscosity of the mixture on the assumption that all collisions are as effective as in a single gas: the result will be correct for a mixture of gases of equal molecular masses, and will be suitable for adaptation to the case where the molecular masses are different. For the rest of the viscosity due to the molecules of 2 we can write a similar expression to that just given, and get

$$\eta = \frac{n_1 m_1 v_1^2}{6(_1\nu_1 + _1\nu_2)} + \frac{n_2 m_2 v_2^2}{6(_2\nu_2 + _2\nu_1)}; \quad \cdot \quad \cdot \quad \cdot \quad (6)$$

while for each ingredient of the mixture we have

$$\eta_1 = \frac{n_1 m_1 v_1^2}{6\,_1\nu_1}, \qquad \eta_2 = \frac{n_2 m_2 v_2^2}{6\,_2\nu_2}. \quad \cdot \quad \cdot \quad \cdot \quad (7)$$

But $m_1 v_1^2 = m_2 v_2^2$ and $m_1 \kappa_1^2 = m_2 \kappa_2^2$, and the equations given suffice for the elimination of everything but the η's, m's, and n's; thus

$$\eta = \frac{\eta_1}{1 + \dfrac{n_2}{4n_1}\{1 + (\eta_1 m_2^{\frac{1}{2}}/\eta_2 m_1^{\frac{1}{2}})^{\frac{1}{2}}\}^2 \left(\dfrac{m_1 + m_2}{2m_2}\right)^{\frac{1}{2}}}$$
$$+ \frac{\eta_2}{1 + \dfrac{n_1}{4n_2}\{1 + (\eta_2 m_1^{\frac{1}{2}}/\eta_1 m_2^{\frac{1}{2}})^{\frac{1}{2}}\}^2 \left(\dfrac{m_1 + m_2}{2m_1}\right)^{\frac{1}{2}}}. \quad (8)$$

So far our equations have related to forceless smooth perfectly restitutional spherical molecules; but as it has been

shown (Phil. Mag., Dec. 1893) that the effect of molecular attraction in the viscosities of gases and allied phenomena is important, we must take account of it here. It was also shown (Phil. Mag., Dec. 1893, and July 1894) that molecular attraction can be taken account of by replacing $(a_1+a_2)^2$ and $(a_1+a_1)^2$ in such equations as (3) and (4) by

$$(a_1+a_2)^2(1+{_1}C_2/T) \text{ and } (a_1+a_1)^2(1+{_1}C_1/T),$$

where ${_1}C_2$ depends only on the mutual potential energy of a 1 and a 2 in contact, and ${_1}C_1$ on the potential energy of a 1 and a 1, and T is the absolute temperature. On introducing the factors $1+{_1}C_2/T$, $1+{_1}C_1/T$, and $1+{_2}C_2/T$ into equations (3) and (4) and eliminating as before, we obtain the equations

$$\left.\begin{aligned} \eta &= \frac{\eta_1}{1+\alpha_1 n_2/n_1} + \frac{\eta_2}{1+\alpha_2 n_1/n_2}, \text{ where } \alpha_1 \text{ is similar to } \alpha_2, \\ \text{and} \\ \alpha_1 &= \frac{1}{4}\left\{1+\left(\frac{\eta_1 m_2^{\frac{1}{2}}(1+{_1}C_1/T)}{\eta_2 m_1^{\frac{1}{2}}(1+{_2}C_2/T)}\right)^{\frac{1}{2}}\right\}^2 \left(\frac{m_1+m_2}{2m_2}\right)^{\frac{1}{2}} \frac{1+{_1}C_2/T}{1+{_1}C_1/T} \end{aligned}\right\} \quad (9)$$

to replace (8) when molecular attraction is taken account of If α_1 and α_2 were each unity this equation would reduce to $(n_1+n_2)\eta = n_1\eta_1 + n_2\eta_2$, which Graham found empirically to be true within the limits of experimental error for mixtures of N_2 and O_2, CO and O_2, and CH_4 and O_2, but not for mixtures containing H_2. Thus we see that the simplicity of Graham's result for these pairs of gases is the result of what may be called an accidental simplification of the true relation, brought about by a certain accidental approximate relation between certain physical constants of the two gases of each pair.

Let us write the last formula in the form

$$\eta = \frac{\eta_1}{1+{_1}v_2/{_1}v_1} + \frac{\eta_2}{1+{_2}v_1/{_2}v_2}; \quad \cdots \quad (10)$$

and we can see that, as regards the general case of any two gases, its defect consists in making each of the ${_1}v_2$ encounters just as effective in producing viscosity as each of the ${_1}v_1$ or ${_2}v_2$. According to the ordinary mode of presenting the theory of viscosity of a single gas, which has already been sketched, it is not easy to see exactly how serious the defect may be or how it is to be remedied. But there is another method of regarding viscosity according to which we get more at the heart of the process.

In a single gas the average distance normal to the solid planes travelled by a molecule is $\lambda/2$, so that the molecules which collide in any thin layer may be considered as coming

from distances $\lambda/2$ parallel to the axis of x on opposite sides of the place of collision with velocities $w\lambda/2D$ and $-w\lambda/2D$ relative to the layer at x which moves with its permanent velocity xw/D. Now the total number of encounters occurring in unit time in unit volume of the layer is $nv/2$, of which half will occur between the molecules of the two sets, and the other half between the members of each set amongst themselves. The average value of the momentum communicated to one another by the molecules colliding with opposite velocities α and α is $2(\alpha+\alpha)mm/3(m+m)$, so that while a molecule brings in momentum $m\alpha$ to the layer, it loses on the average at the first collision only $2m\alpha/3$; thus, after one collision between each pair of molecules the distribution of velocities may be represented by evenly distributed radii of a sphere to represent the evenly distributed average velocities v, then with half of these velocities taken at random compound a velocity $w\lambda/6D$ in the direction of w, and with the other half at random compound a velocity $-w\lambda/6D$, so that the original spherical surface is resolved into two having their centres displaced in opposite directions by a distance representing $w\lambda/6D$. According to the usual method of presenting the theory of the viscosity of a gas, this distribution is assumed to be identical with that represented by the undisplaced sphere, and the assumption is plausible when it is remembered that the small variations introduced by compounding the small velocities $w\lambda/12D$ and $-w\lambda/12D$ with the average velocity v may be merged in the much larger variations represented by Maxwell's law of the velocities which we have ignored in considering only average velocities. And yet an assumption which makes the effect of an encounter practically independent of the amount of momentum communicated by the colliding molecules to one another must be erroneous, and must affect the usual expressions for viscosity with an error appearing in the value of the numerical coefficient. As each collision is only two thirds as effective in communicating momentum as it is assumed to be in the ordinary theory, we ought, in the usual expressions for the viscosity, to introduce an additional numerical factor $2/3$, which would cause the value of the mean free path of a gas as calculated from its experimental viscosity to be $3/2$ of the value usually given.

With this principle, that the effective value of a collision is proportional to the momentum exchanged by the colliding molecules, we can adapt our equation (9) to the general case of mixed gases by replacing $_1\nu_2/_1\nu_1$ by $(_1\nu_2/_1\nu_1)(_1\mu_2/_1\mu_1)$, where $_1\mu_1$ and $_1\mu_2$ are the average momenta exchanged when 1

collides with 1 and with 2 ; and we have now to obtain expressions for these momenta. I have not succeeded in doing this from first principles, but by the study of Graham's experimental data have been led to a simple result allowing of very simple interpretation, namely, that if in expression (9) the coefficients α_1 and α_2 are multiplied respectively by

$$\{2m_2/(m_1+m_2)\}^{\frac{3}{4}} \quad \text{and} \quad \{2m_1/(m_1+m_2)\}^{\frac{3}{4}},$$

all the experimental results can be represented by the formula so derived, namely,

$$\eta = \frac{\eta_1}{1+\beta_1 n_2/n_1} + \frac{\eta_2}{1+\beta_2 n_1/n_2}, \quad \text{where } \beta_2 \text{ is similar to } \beta_1,$$
and
$$\beta_1 = \frac{1}{4}\left\{1+\left(\frac{\eta_1 m_2^{\frac{1}{2}}(1+{}_1C_1/T)}{\eta_2 m_1^{\frac{1}{2}}(1+{}_2C_2/T)}\right)^{\frac{1}{2}}\right\}^2\left(\frac{2m_2}{m_1+m_2}\right)^{\frac{1}{4}}\frac{1+{}_1C_2/T}{1+{}_1C_1/T}.$$

$$\biggr\}\ (11)$$

Thus the ratio ${}_1\mu_2/{}_1\mu_1$ is represented by $\{2m_2/(m_1+m_2)\}^{\frac{3}{4}}$, and we can easily trace the origin of the form of this ; for the momentum exchanged in an average collision between an m_1 and an m_2 with velocities α_1 and α_2 being

$$2(\alpha_1+\alpha_2)m_1m_2/3(m_1+m_2),$$

and between an m_1 and an m_1 being $2m_1\alpha_1/3$, the ratio of the two is $\{2m_2/(m_1+m_2)\}\{(\alpha_1+\alpha_2)/2\alpha_1\}$; and if this is equal to $\{2m_2/(m_1+m_2)\}^{\frac{3}{4}}$, then $(\alpha_1+\alpha_2)/2\alpha_1 = \{2m_2/(m_1+m_2)\}^{\frac{1}{4}}$, but if ${}_1V_2{}^2$ and ${}_1V_1{}^2$ are the average squared relative velocities of a 1 and a 2, and of a 1 and a 1, then

$$\overline{{}_1V_2{}^2}/\overline{{}_1V_1{}^2}) = (\kappa_1{}^2+\kappa_2{}^2)/2\kappa_1{}^2 = (m_1+m_2)/2m_2,$$
$$\therefore\ (\alpha_1+\alpha_2)^2\{\overline{{}_1V_2{}^2}\}^{\frac{1}{2}} = (2\alpha_1)^2\{\overline{{}_1V_1{}^2}\}^{\frac{1}{2}};$$

so that if $(\alpha_1+\alpha_2)^2$ and $(2\alpha_1)^2$ are regarded as quantities which are being carried across the mixed gas with average velocities proportional to ${}_1V_2$ and ${}_1V_1$, then the final meaning of our result is that they are carried at the same rate.

We have now to show how closely (11) represents the experimental facts, and with that view Graham's results are reproduced in the following tables from the Phil. Trans. 1846, or his collected Chemical and Physical papers, along with the necessary data for use in equation (11) and the results given by that equation. The necessary data are the viscosities of the two pure gases which are measured by Graham at temperatures near 15° C., and were given by him in terms of that for oxygen at the same temperature as unity, also the molecular masses referred to that of H_2 as 2, and finally the

values of the constants $_1C_1$, and $_2C_2$, and $_1C_2$ as given in the Phil. Mag. Dec. 1893 and July 1894, or calculated on the principles there given.

Viscosity of Mixtures.

CO_2 and H_2.

	η_1. .751	η_2. .450	m_1. 44	m_2. 2	$_1C_1$. 277	$_2C_2$. 53	$_1C_2$. 115
n_1/n_2			9	3	1	1/3	1/9
η experiment			.753	.752	.734	.679	.572
η calculated			.752	.752	.736	.671	.574

CO and H_2.

	η_1. .870	η_2. .450	m_1. 28	m_2. 2	$_1C_1$. 100	$_2C_2$. 53	$_1C_2$. 70
n_1/n_2			19	9	3		
η exper.			.865	.865	.843		
η calcul.			.863	.858	.835		

CH_4 and H_2.

	η_1. .550	η_2. .450	m_1. 16	m_2. 2	$_1C_1$. 215	$_2C_2$. 53	$_1C_2$. 102		
n_1/n_2	39	19	9	4·7 · 3	1	1/3	1/9	1/19	1/39
η exper.	.550	.561	.563	.557 · .559	.560	.531	.496	.480	.471
η calcul.	.551	.552	.552	.556 · .556	.554	.528	.494	.473	.473

Air and H_2.

	η_1. .900	η_2. .450	m_1. 28·9	m_2. 2	$_1C_1$. 113	$_2C_2$. 53	$_1C_2$. 74·5	
n_1/n_2		19	9	3	1	1/3	1/9	1/19
η exper.		.896	.889	.879	.820	.719	.588	.528
η calcul.		.893	.888	.864	.801	.685	.566	.511

CO_2 and O_2.

	η_1. .751	η_2. 1·0	m_1. 44	m_2. 32	$_1C_1$. 277	$_2C_2$. 127	$_1C_2$. 187	
n_1/n_2		19	9	3	1	1/3	1/9	1/19
η exper.		.756	.768	.807	.871	.942	.976	.987
η calcul.		.762	.773	.807	.867	.931	.974	.984

O_2 and CH_4.

	η_1. 1·0	η_2. .550	m_1. 32	m_2. 16	$_1C_1$. 127	$_2C_2$. 215	$_1O_2$. 165
n_1/n_2			1	1/3	1/9		1/19
η exper.			.808	.690	.598		.583
η calcul.			.781	.667	.597		.573

O_2 and N_2.

	η_1. 1.0	η_2. ·875	m_1. 32	m_2. 28	$_1C_1$. 127	$_2C_1$. 109	$_1C_2$. 117
n_1/n_2			1	1/2	1/3	—	1/9
η exper.			·935	·914	·905		·885
η calcul.			·937	·916	·905		·887

O_2 and CO.

	η_1. 1.0	η_2. ·870	m_1. 32	m_2. 28	$_1C_1$. 127	$_2C_2$. 100	$_1C_2$. 113
n_1/n_2			3	2	1	1/2	1/3
η exper.			·967	·959	·936	·913	·904
η calcul.			·967	·957	·933	·912	·900

The only pairs of gases for which Graham's data have not been given are N_2O and H_2 and NO and H_2, but the physical constants for N_2O are almost identical with those for CO_2, and the viscosities of its mixtures are almost the same as those of mixtures of CO_2 ; for NO some of the data necessary for the calculation are lacking.

Puluj measured the viscosities of a large number of mixtures of CO_2 and H_2 by the method of the vibrating disk (*Sitzb. Akad. Wien*, lxxix.), giving the absolute values at $14^\circ{\cdot}7$ C.; thus η_1 is ·000147 and η_2 is ·000089 ; the other constants required in the calculation remain as above, and we have the following comparison of experiment and calculation values of $10^6\eta$:—

n_1/n_2 ...	9	4	2·6	·77	·36	·19	·11	·068	·04	·025	·017
Exper....	148	149	150	148	140	131	122	111	103	99	96
Calcul....	147	147	147	142	133	122	113	106	100	96	94

The agreement between the formula (11) and experiment is not so good here as in Graham's mixtures of CO_2 and H_2, which means that there are discrepancies between Graham's and Puluj's measurements ; these are probably due to slight impurity to which the viscosity of hydrogen is sensitive. But even if the agreement is not good in the details of the last comparison, the main phenomenon of the experiments is closely paralleled by the formula, for in the results both of experiment and formula the addition of one volume of hydrogen to 2·6 volumes of carbonic dioxide hardly affects the viscosity of the carbonic dioxide.

The case of CH_4 and H_2 in the previous comparison is the most interesting, as both experiment and the formula make the viscosity of a mixture of equal volumes of the two gases greater than that of pure CH_4. It must be remembered that

the formula (11) has not been obtained from purely dynamical first principles, but in addition to the usual dynamical principles of the kinetic theory involves two unproved assumptions —first that formula (10), which applies rigorously to a mixture of two sets of molecules of equal mass but unequal size, can be adapted to the case of two sets of unequal mass and size by replacing the ratios $_1\nu_2/_1\nu_1$ and $_2\nu_1/_2\nu_2$ by $_1\nu_2\,_1\mu_2/_1\nu_1\,_1\mu_1$ and $_2\nu_1\,_2\mu_1/_2\nu_2\,_2\mu_2$, where $_1\mu_1$ and $_1\mu_2$ are the average momenta exchanged when 1 collides with 1 and with 2 ; and second, that the relative molar velocity of collision of a 1 with a 2, namely, $\alpha_1 + \alpha_2$, is connected with the relative molar velocity of collision of a 1 with a 1 $(2\alpha_1)$ by the equation

$$_1\overline{V}_2(\alpha_1 + \alpha_2)^2 = {}_1\overline{V}_1(2\alpha_1)^2,$$

where $_1\overline{V}_2$ and $_1\overline{V}_1$ are the mean relative molecular velocities of a 1 and a 2 and of a 1 and a 1. A dynamical proof of these two assumptions is required before the foregoing dynamical theory of the viscosity of mixed gases can be considered complete.

Melbourne, March 1895.

XXXVIII. *The Thermal Unit.* By E. H. GRIFFITHS, *M.A.,* *F.R.S., Sidney Sussex College, Cambridge**.

[Plates VI. & VII.]

[The following Paper was read at the Ipswich Meeting of the British Association. The consideration of the whole matter has now been referred to the Committee on Electrical Standards.

The Author would be glad to receive any practical suggestions with a view to their communication to that Committee.]

INTRODUCTORY NOTE.

THE majority of physicists will, I think, agree with the statement that our present system of thermal measurements rests on an unsatisfactory basis. Nevertheless the attitude of the scientific world regarding this matter appears to be one of indifference ; and it is open to speculation whether this indifference arises from non-appreciation of the importance of the subject, or from a sense of the difficulties to be encountered if any action is taken.

I am glad of this opportunity of directing the attention of Section A to such an important question, for I believe the obstacles to progress are not insurmountable, provided they are attacked with the same spirit and energy which characterized the efforts of this Association to perfect our system of electrical measurements. The prevailing apathy is possibly

* Communicated by the Author.

due in some measure to a comfortable belief in the validity of any conclusions arrived at by Regnault. The disciples of science are often accused by the public of a lack of reverence for tradition and authority, but my own experience leads me to the belief that no class is more conservative. If the name of a master of our craft is at any time associated with some conclusion or numerical value, even his own subsequent corrections and amendments are liable to pass unregarded. Numerous instances could be cited : as, for example, the result of Joule's own comparison of his thermometer with Rowland's ; or, again, Regnault's statement of his doubts concerning his conclusions as to the Latent Heat of Evaporation of Water at low temperatures.

Our feelings of veneration for great men and our admiration of their work are, however, carried to harmful excess when they act as a check on the criticism and revision of the numerical results of their experiments. Since the year 1879, when Rowland published his monumental work on the mechanical equivalent, there can, I think, be no doubt in any unbiassed mind that Regnault's expression for the capacity for heat of water is inaccurate at temperatures below $30°$. Yet we find the most recent books of reference ignoring the researches of Rowland, and still reducing thermal quantities to that impossible unit " the capacity for heat of water from $0°$ to $1°$ " by means of Regnault's formula.

My object in the first part of this paper will be to show how vague and uncertain is our knowledge of the changes in the capacity for heat of water as its temperature varies. I shall not attempt to consider at any length the work of all the investigators who have attacked this problem, but shall be guided by one general principle in my selection ; viz., that however admirable the methods of experiment, or however sound the theories on which they are based, the numerical results are useless unless the observer has devoted sufficient attention to the measurements of temperature. The force of this argument will be more evident when it is remembered that the experiments which give the most rapid decrease in the capacity for heat of water at low temperatures (viz. those by Rowland) would show an increase if the results were expressed on the mercury- instead of the air-scale. It might appear from this statement that if the changes are so small they may be unimportant ; but it must be borne in mind that in the reduction of the thermal quantities we have, as a rule, to deal with the summation of such changes over large ranges of temperature (as, for example, in " the method of mixtures "), hence the effect may be, and often is, considerable.

PART I.

The Capacity for Heat of Water at Different Temperatures.

From the time of Black to the present day no practical thermal standard, except the capacity for heat of water, has been adopted. Its capacity at 0°, 4°, 15°, and its mean capacity from 0° to 100°, have been variously selected as standards by different observers ; and since our knowledge of the comparative value of these standards is vague, to say the least of it, comparison of the results of the different investigators becomes impossible. A consequent evil is the growth of a specious accuracy : books of reference give the changes in the specific heat of various bodies, as for example mercury, to 4 or 5 significant figures*, whereas our knowledge of the standard in which they are expressed is far less exact. I give the following illustration as an example. Last year I communicated to this Section the results of an inquiry into the changes in the specific heat of Aniline due to changes in temperature. The conclusions there given depended on a method which, whatever may have been its merits, was at all events an absolute one in the sense that the results were independent of the changes in the thermal properties of water. In the following autumn Mr. C. Green made a series of careful determinations of the density of aniline over the same range of temperature. An interesting and unexpected relation then became evident, viz., that the " volume heat " of aniline over the temperature-range 20° to 50° might be regarded as constant †. I was naturally anxious to see if this relation held in the case of any other body ; but I have been unable, in spite of diligent search, to find any determinations of specific heat which are independent of some assumption with regard to the changes in the capacity for heat of water. This example is sufficient to show how inquiry is checked by our present uncertainties.

It appears to me that we have been singularly unfortunate in the selection of the capacity for heat of water as our standard. At the same time our whole system of thermal measurements has become so intimately connected with the heat-capacity of that liquid that it would require nothing short of a revolution to abolish its use as a standard : the laboratory might consent but the workshop would rebel. Under such circumstances we must make the best of the

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* See Landolt.
† Proc. Camb. Phil. Soc., 1895.

position in which we find ourselves, and our first step should be to apprehend clearly the nature of the difficulties with which we have to contend.

The first experiments of any accuracy on this subject seem to have been those of Newman in 1831[*], who found the specific heat of water at boiling-point to be 1·0127 times that at 28°.

Regnault in 1840 found the "mean thermal unit" to be 1·00709 and 1·00890 times that at about 14° C. His principal experiments, however, were those published in 1850[†], with regard to which Rowland remarks as follows[‡] :—"It is unfortunate that those experiments were all made by mixing water above 100° with water at ordinary temperatures, *it being assumed that water at ordinary temperatures changed little, if any.* An interpolation formula was then found to represent the results, and it was assumed that the same formula held at low temperatures, even as low as 0° C."

The assumption thus referred to by Rowland would alone be sufficient to render of little value the conclusions arrived at by Regnault regarding the changes at low temperatures.

Mr. Macfarlane Gray[§] has called attention to the fact that there must be some error in the tables given in Regnault's paper, for the columns of data do not agree with the column of results. Wüllner[||] accepts the data columns as correct, and from the re-calculation concludes that the specific heat of water may be taken as constant up to 190° C. Mr. Macfarlane Gray, however, considers that the error is in the statement of the data, but that Regnault calculated his results from correct data. He is led to this conclusion by the fact that the sum of the weights of the hot and cold water seems in all the doubtful experiments to be greater than the capacity of the calorimeter. On page 452, *ibid.*, is given an account of a careful examination, made by Professor Ryan and Mr. Gray, of Regnault's apparatus which appears to bear out the conclusions arrived at by Mr. Gray. Whichever view is correct, it is obvious that there is a discrepancy in the numbers as published. Boscha has attempted to correct Regnault's results, but, in *Comptes Rendus,* Regnault has not accepted the correction.

[*] Pogg. *Ann.* xxiii. p. 40.
[†] Pogg. *Ann.* lxxix. p. 241 ; and " De la Chaleur Specifique," *Acad. des Sciences,* tome xxi.
[‡] Proc. American Acad., vol. xv. p. 120.
[§] Proceedings Mechanical Engineers, July 2, 1889, p. 401.
[||] *Exper. Physic.*, 1885.

Hirn* has made some experiments on the specific heat of water at low temperatures, which give the extraordinary result that its capacity for heat increases by about 6 per cent. between 0° and 15°. Rowland's comment on these is as follows †:—"Experiments so full of error only confuse the physicist and are worse than useless."

Jamin and Amaury made some determinations by the heating of water by an electric current. Their experiments were good in principle, but no precautions were taken with regard to the measurement of temperature, which they regarded as a simple matter; their results, therefore, are of no value.

Pfaundler and Platter ‡ found variations as great as 20 per cent. between 0° and 10°! Shortly afterwards, however, they published another paper which showed that the former experiments were entirely erroneous. Their second series showed an increase to 6° and a decrease to 13°, but their temperature measurements were based entirely on a Geissler thermometer.

The experiments of M. von Münchausen § were performed in an open vessel, and no reference is made to the thermometry.

In 1879 Rowland published the results of his remarkable series of experiments. The attention given by him to the standardization of his thermometers and the perfection of his experimental methods render his results of extreme value. His experiments extended from 5° to 34° C.; and if we accept the validity of his thermometry, they establish beyond question a decrease in the capacity for heat of water over nearly the whole of that range, and appear to indicate a minimum about 30° to 32° C. In addition to his determinations by mechanical means, he performed a series by a direct method of mixtures which led to a somewhat similar conclusion, except that the rate of decrease was less.

The recent investigations of Bartoli and Stracciati ‖ also indicate a decrease in the capacity up to 20°, about which temperature they find a minimum, although even over that range their rate of decrease is less than Rowland's. I have already published a brief criticism of their work ¶, in which I give my reasons for the conclusion that their experimental

* *Comptes Rendus,* lxx. pp. 592 and 831.
† Proc. American Academy, vol. xv. p. 121.
‡ Pogg. *Ann.,* 1870.
§ *Journal de Physique,* 1878.
‖ *Ibid.* Dec. 1893.
¶ Science Progress, April 1894.

evidence does not justify the use of the formula given by them. This adverse opinion has been strengthened by some charts, brought under my notice by Mr. Spencer Pickering, F.R.S., which show with great clearness the discrepancy between the results obtained by those observers when using different methods of experiment. It is, however, noticeable that in addition to using thermometers standardized by the Bureau International, they also used a thermometer standardized by Rowland, and no systematic difference is observable in the conclusions drawn from the employment of the different standards. It would therefore appear as if the discrepancy between their conclusions and those of Rowland could not be explained, as is usually the case in such investigations, by a difference in the thermometric standards employed, but that it must arise from experimental errors.

A further indirect comparison of Rowland's air-thermometer with the nitrogen standard of the Bureau International is given in Professor Schuster's paper on the scale value of Dr. Joule's thermometers[*]. The result indicates a difference of about $0°\cdot05$ in elevation over the range $10°$ to $30°$ C., although near the bottom and top of the range the difference alters but slightly.

		1st Series.	2nd Series.
At 10° it is about . .		·025	—
„ 15° „	. .	·045	·045
„ 20° „	. .	·042	·051
„ 25° „	. .	·038	—

These results, however, are dependent upon previous observations made by Joule when comparing his thermometer with Rowland's. As we have no details concerning this comparison, Professor Schuster points out that " it would be necessary to have further information before any definite conclusions can be drawn" (*ibid.* p. 499). Assuming the validity of the above corrections, they would indicate that Rowland's rate of decrease in the capacity for heat of water over the above range is slightly too large.

The most recent determination with which I am acquainted is my own completed in 1892. The method adopted was an electrical one, and singularly suitable for an investigation into the changes in the thermal capacity of water. Errors in the assumptions as to the magnitude of the various constants which would affect the value of J would leave unaltered the relative thermal capacities of water at different temperatures.

* Phil. Mag., June 1895.

The conclusion arrived at was as follows :—" That over the temperature range 15° to 26° (nitrogen scale), the capacity for heat of water, in terms of its capacity at 15°, is (approximately)

$$1 - \cdot000266 \, (\theta - 15)."$$

The function, however, is not absolutely linear, as the rate of decrease diminishes slightly above 22°. During the reading of a communication to the Royal Society in November[*] last, Professor Schuster stated that although the temperature range covered by the experiments by Mr. Gannon and himself was small, the *change* over that range was similar to that resulting from my experiments.

Plate VI. shows the discrepancy, over the range of temperature 10° to 30°, between the results of those observers whose work appears to be most worthy of attention. I have added Regnault's values, for although his conclusions with regard to the changes at this range are undoubtedly erroneous, they are so generally accepted as to render their inclusion important. The results of each observer are expressed in terms of his own value at 15° as unity. A study of the diagram will show that if the results of thermal experiments at 20° were expressed in terms of the "thermal unit at 10°" by means (a) of Regnault's formula, (b) of Rowland's curve, the resulting differences would be as great as 1 in 300 !—an error of serious dimensions when we consider the smallness of the temperature range.

The range 10° to 30° is of particular importance, as the majority of thermal determinations are expressed in terms of the capacity of water at some point within this range, and as a consequence great attention has been devoted to it. The diagram shows that, nevertheless, the results are by no means satisfactory.

The difficulty is one not so much of experiment as of the measurement of temperature, and I would repeat that any one of the results which shows a *decrease*, when expressed in the nitrogen, would show an *increase* if expressed in the mercury scale. Before, therefore, any satisfactory conclusion as to the behaviour of water can be arrived at, it is necessary to decide upon and establish some standard temperature scale. Further refinements in experiment are useless until a general agreement as to temperature measurements has been established.

As an illustration, I may mention that in July I wrote to ask Dr. Guillaume if he would favour me with his opinion on

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[*] Proc. Roy. Soc., November 1894.

this question of the capacity for heat of water as the thermal standard. His answer was to the effect that the French physicists did not feel that the problem could be profitably attacked until some general agreement was arrived at with regard to the scale of temperature to be adopted.

The determinations of the capacity for heat of water at higher temperatures are still more uncertain than those below 30°. Many attempts have been made to solve the difficulty by the use of Bunsen's calorimeter. Concerning these experiments Dieterici writes as follows * :—" The great differences which are shown by observations carried out in this manner render it probable that this instrument is unsuitable for the purpose." Now no one has been more successful in the use of this apparatus than Dieterici himself (*vide* his determination of L and J by such means), and his opinion therefore carries great weight.

For example, Velten†, who performed a very elaborate series of determinations with Bunsen's calorimeter, finds a maximum in the capacity of water between 0° and 7°; from 7° to 10° a decrease, from 10° to 20° an increase, then a decrease to 40°, where it reaches a minimum, then rises to 70° and remains constant to 100°!

Difficulties with regard to the measurement of *temperature* are, however, much diminished by the use of Bunsen's calorimeter, and the conclusions of different observers as to the amount of mercury drawn into the instrument by unit mass of water when cooling from 100° to 0° are in fair agreement. For example : —

<div style="text-align:center">

Bunsen . . . . . . 15·41
Schüller and Wartha . . 15·442
Velten . . . . . . 15·47‡

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and hence Bunsen, Schüller and Wartha, Wüllner, and Dieterici strongly advocate the adoption of this "mean calorie" as the thermal unit§.

With regard to this proposal I would remark that the discrepancy between the above standard determinations amounts to 1 in 250, and further, that even if the relation between the heat developed and the weight of mercury is capable of exact determination, the unit thus adopted would be useless unless we knew its relation to the thermal unit "at a temperature $t°$;" for all thermal determinations cannot

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* Wied. *Ann.* xxxiii. p. 444 (1888).
† *Ibid.* viii. p. 83 (1879).
‡ *Ibid.* xxxiii. p. 439 (1888).
§ *Ibid.* xxxiii. p. 431.

be conducted by means of Bunsen's calorimeter, and thus no advance would be made towards the solution of the difficulty in which we are placed by the existing uncertainty regarding the heat-capacity of water at different temperatures.

The value of the "mean calorie" in terms of a "thermal unit at $t°$" has been indirectly investigated by Dieterici. His determination * of the value of J has, I think, received far less attention than so important a communication deserves. His value is $4·2436 \times 10^7$ † in terms of the "mean calorie" ‡; and he points out that this result is in fair agreement with Rowland's, if we make the following assumptions (*ibid.* p. 422) :—

(1) That the capacity for heat of water changes between 0° and 5° in the same linear manner as given by Rowland's observations from 5° to 30°.

(2) That the capacity from 30° to 100° changes linearly with the temperature.

If we assume number (1) and hence deduce Rowland's value of J at 0°·5, then (using Dieterici's corrected value) :—

$$\frac{\text{Mean calorie}}{\text{Thermal unit at } 0°·5} = \frac{\text{Dieterici's value of J}}{\text{Rowland's value at } 0°·5} = \frac{4·233}{4·224} = 1·002,$$

as against 1·005, the value of the same ratio according to Regnault.

If we apply the same method to determine the ratio

$$\frac{\text{Mean calorie}}{\text{Thermal unit at } 15°} \text{ we get } \frac{4233}{4189} = 1·010, \text{ as against}$$

$\frac{1·005}{·992} = 1·013$, the value obtained from the experimental

numbers of Regnault and Rowland. The discrepancies are thus comparatively small.

It appears to me, however, that if we make the assumptions mentioned by Dieterici (*supra*, 1 and 2) we are "begging the whole question." As Rowland remarks §, "The specific heat of melting ice is infinite. Why is it necessary that the specific heat should instantly fall and then recover? ... We have physical evidence that the water has not recovered its natural condition until above 4° C."

In a recent communication to the Royal Society ‖ I gave

* Wied. *Ann.* xxxiii.
† *Tom. cit.* p. 418.
‡ A necessary correction, of which I give particulars later, reduces this to $4·233 \times 10^7$.
§ Proc. American Acad., vol. xv. p. 131.
‖ Phil. Trans. clxxxvi. (A) 1895, pp. 316–323.

experimental reasons for the conclusion that the ratio $\frac{\text{Mean calorie}}{\text{Thermal unit at } 15^\circ}$ is much nearer unity than the result of the above comparison would indicate. I cannot here do more than briefly state the reasons for my conclusions, but full details of the experimental evidence will be found by any who refer to the original paper. I performed some experiments on the latent heat of evaporation of water at temperatures 25°, 40°, and 50°, and, having made improvements in the apparatus, determined with great care the value of L at 30° and 40°.

The result of all these experiments is closely represented by the formula

$$L = 596{\cdot}73 - 0{\cdot}6010\,\theta$$

in terms of a thermal unit at 15° C.

Now if we assume $\dfrac{\text{Mean calorie}}{\text{Thermal unit at } 15^\circ} = 1{\cdot}0115$ (mean of results given *suprà*), the value of L at 0° as determined by Dieterici is 603·6, whereas if we assume the *equality* of the two units Dieterici's value becomes 596·73, *i. e.*, is identical with that resulting from my experiments.

Again, if we deduce the values of L over the range 63° to 100° from Regnault's experiments on the Total Heat of Steam, then (assuming as before the equality of the two thermal units) the above formula represents, with extraordinary accuracy, the result of Regnault's experiments.

This evidence is of course indirect, but, at the same time, its weight cannot be rightly estimated without a study of the Tables XIV. to XVII., as given in the above paper.

The abstract of that communication came under the notice of Dr. Joly, F.R.S., who thereupon commenced a series of determinations by means of his well-known calorimeter. A short account of the experiments and the conclusions to which they led is given by Dr. Joly in pp. 322, 323 of my paper. These experiments are, I believe, the first direct determinations of the ratio of the mean calorie to the thermal unit at 15° which have been performed since the time of Regnault; and I may be permitted to express my gratification at the extent to which they bear out my predictions of December 1894, regarding the close equality of the two units. The result is :—

$$\frac{\text{Mean calorie}}{\text{Thermal unit at } 15^\circ} = \frac{0{\cdot}9957*}{1}.$$

* In obtaining this number Dr. Joly assumed the decrease from 0° to 15° given by Bartoli and Stracciati; if we assume Rowland's decrease over that range we get 0·9962.

We thus see that the determinations of this ratio vary from 1·013 to ·9957, a difference of one part in 60, and an additional uncertainty is introduced by the differences of 1 in 250 above referred to in the determinations by Bunsen, Schüller and Wartha, and Velten, as to the weight of mercury corresponding to the " mean calorie."

I think the considerations adduced in the preceding pages are sufficient to justify the statement that our endeavours to establish the capacity for heat of water as the standard of calorimetric measurements have, so far, not met with success. Nevertheless progress is essential. Whatever may be the calorimetric standard adopted, it will still be necessary to obtain more exact information concerning the changes in the capacity for heat of water, otherwise the reduction of the results of different observers to some common standard will remain an impossibility. I believe that the obstacles are now not insurmountable. Recent advances in the methods of calorimetry and thermometry have placed more efficient instruments at our disposal. For example, the use of differential platinum thermometers does away with many of the difficulties hitherto connected with the measurement of small changes of temperature, and, I would venture to add, the method which I found efficient when tracing the changes in the specific heat of aniline is *mutatis mutandis* applicable in the case of water.

It is now chiefly a financial difficulty which blocks the way, for the apparatus would have to be on a large scale and necessarily expensive.

If this Association could see its way to provide that apparatus and capable hands to work it, I believe our present doubts would soon be dispelled and be replaced by a reasonable certainty.

Part II.

Consideration of certain Thermal Units other than those dependent on the Capacity for Heat of Water.

In the paper by Mr. Macfarlane Gray, previously referred to, he defines his unit of heat as follows :—" That quantity of constitutional molecular energy which is mechanically equivalent to the variation of the pv product for the unit mass of hydrogen gas per degree, at the temperature of melting ice and atmospheric pressure."

Mr. Gray gives the mechanical equivalent of this unit of heat as 422·45 kilogramme-metres, but I differ from him considerably in the numerical value of this constant*.

* My own calculations of this quantity give 429·17 kilogramme-metres.

He adds, " Even if the specific heat of water was accurately known it would not, for any reason, be arithmetically commensurable with any other definite physical quantity. Hydrogen is an elementary substance, and its atomic weight is a standard unit in the arithmetic of chemistry. The specific pv of hydrogen is on this account most appropriate for the standard unit of heat and energy in the arithmetic of thermodynamics."

Although there is much force in Mr. Gray's arguments, there are, however, practical objections. The exact determination of pv presents almost similar difficulties to those encountered in the determination of the capacity for heat of water. We are entirely dependent on thermometric measurements, and I doubt if we have yet thoroughly mastered the difficulties of gas thermometry, more especially as regards the influence of the envelope on the enclosed gas. The theoretical advantages are no doubt great, but the practical difficulties would I believe be increased instead of diminished by the adoption of this unit.

In a letter to 'Nature,' May 2, 1895, Dr. Joly suggests the latent heat of steam at the standard pressure as a practicable unit. He remarks as follows :—" One gramme of saturated steam at 760 millim. might be assumed to give up the unit quantity of heat in becoming water without change of temperature. This unit might be called a therm, in order to avoid confusion with the existing unit. The specific heat of water would then stand at about 1·8 milli-therms. The larger value of the new unit commends itself as being more applicable to the problems of applied science ; which, indeed, may be inferred from the fact that engineers often understand by the term calorie the kilogramme-degree.

" I am aware that the change proposed is a radical one ; but an appreciable change is better than a vexatious correction, and we know now that revision and change are inevitable.

" In the definition of the proposed unit we replace the unreliable thermometer by one of the most trustworthy of instruments—the barometer ; and our quantities of heat may be determined by the chemical balance, and at 760 millim., read directly upon the weights. We are sure of the purity of the material."

This appears to me to be a thoroughly practical suggestion, and, above all, it clears the way of many of the difficulties connected with thermometry. The change, however, is I fear too radical and the magnitude of the proposed unit is distinctly inconvenient. I will not dwell on this point, for I have reason to believe, from a conversation I subsequently

had with Dr. Joly, that he is now in favour of some such proposal as that which I have to make at the close of this paper, and I hope to be able to add a promised communication from him as an appendix.

In 'Nature,' May 23, 1895, Mr. Spencer Pickering advocates the adoption of the latent heat of fusion of ice as the unit. He writes as follows :—" A unit of convenient magnitude would be one equivalent to about 100 small calories, and 100 calories has, indeed, been adopted as a unit by more than one writer on thermo-chemistry. There is, however, what may be termed a natural quantity which is nearly equivalent to such a unit, namely, the heat of fusion of one gram. of water at 0° C., which is nearly eighty calories. This appears to be just as suitable from other points of view as the heat of vaporization of one gram of water at constant temperature and 760 millim. pressure ; and if this latter can be recommended on the ground that in defining it we replace the thermometer by the barometer, the former will possess the superior claim of (for all practical purposes) not depending even on the barometer.

" Neither of these proposed units, however, possess what should be the chief characteristic of a physical unit, namely, a simple relation to other units ; and before adopting either of them, it would be well to consider whether some convenient unit related to, say, the electrical units, could not be adopted. A committee of the British Association would be a body most suited to investigate this matter."

I doubt, however, if there is any prospect of ascertaining the value of this "fusion-unit" with sufficient accuracy. Mr. Pickering says " it should be determinable with quite as much accuracy as the latent heat of vaporization;" but here I join issue with him. The attempts which have so far been made to determine this quantity with precision cannot be considered as successful, and I believe that there are great experimental difficulties in the way. When we have come to a general agreement as to the magnitude of this constant, the time may have arrived for a consideration of Mr. Pickering's suggestion. Both the "fusion-unit" and the "vaporization-unit" would, however, be purely arbitrary, and, to repeat the words of Mr. Gray, " would not be arithmetically commensurable with any other physical quantity."

I now pass to the consideration of what appears to me to be the only solution of the difficulty, viz. the adoption of the thermo-dynamic unit. Such a unit is by no means a novelty, for it was in reality made use of by Rowland when tabulating the results of his experiments on the mechanical equivalent,

and more markedly by Professor Schuster and Mr. Gannon when they entitled their recent communication to the Royal Society "The Specific Heat of Water" *. Several objections to this proposal of course immediately present themselves, of which the most important is the want of agreement amongst different observers as to the capacity for heat of water at any given temperature when expressed in terms of such a unit. The divergence is not, however, so great as is usually supposed.

I will not enter at length into my reasons for especially selecting the work of certain observers ; but the principle by which I have been guided is the same as that which influenced my choice of experiments on the changes in water, viz. the attention given to thermometry.

I also consider it necessary to reject results obtained by such electrical methods as are dependent on the measurement of resistance, if the observer has neglected the change in resistance of the conductor consequent on the rise in temperature due to the passage of an electric current.

I propose to select the following :—

(1) The results of the later experiments of Joule, as considered in the light of Professor Schuster's recent exhaustive re-standardization of Dr. Joule's thermometers, Phil. Mag. June 1895. (Mechanical.)

(2) The determinations of Prof. Rowland, 1879. (Mechanical.)

(3) The work of Miculescu. (Mechanical.)

(4) The work of Dieterici. (Electrical.)

(5) My own experiments of 1892. (Electrical.)

(6) Prof. Schuster and Mr. Gannon's results in 1894. (Electrical.)

JOULE.—The results of Joule's later experiments as announced by himself were 772·55 ft.-lbs., *i. e.* $4·162 \times 10^7$ ergs at 61°·7 F. Joule's own comparison with Rowland's thermometer raised this value, after certain corrections by Rowland, to $4·182 \times 10^7$ ergs. During this summer Professor Schuster published an account (Phil. Mag. June 1895) of his elaborate comparison of the Joule thermometers with the nitrogen-scale of the Bureau International. His conclusion is as follows :—
"Joule's equivalent of heat resulting from his own investigation and reduced to the nitrogen-thermometer of the Bureau International, when expressed in ergs, becomes $4·173 \times 10^7$."
(Temperature 16°·5 C.)

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* In the discussion following the reading of this paper, Lord Kelvin remarked that Prof. Rankine had made a similar suggestion.

Rowland.—I have elsewhere expressed my admiration of Rowland's work, and were it not for some doubts regarding the thermometry I should accept his results as conclusive. The investigations by Professor Schuster above referred to " open out the possibility that Rowland's value might have to be reduced somewhat when referred to the Paris air-thermometer."

Professor Schuster's tables, however, indicate that any such possible change would be very small, and the further comparison (already mentioned) by Messrs. Bartoli and Stracciati between Rowland's thermometer and a Tonnelot thermometer from the Bureau International shows the agreement between the two standards to be very close. The results of these investigations modify my previously expressed apprehensions regarding Rowland's thermometry, although I join with Professor Schuster in his desire that more light should be thrown on the matter by a direct comparison of a Rowland thermometer and the International Standard. Rowland's value at 15° is $4 \cdot 1895 \times 10^7$, and at 10°, $4 \cdot 2 \times 10^7$.

Miculescu.—The following is a quotation from Professor Schuster and Mr. Gannon's paper :—" We now turn to an investigation of Miculescu (*Annales de Chimie et de Physique*, vol. xxvii. 1892), in which the mechanical equivalent of heat is measured directly by what seems a very excellently devised series of experiments. Its result is $4 \cdot 1857 \times 10^7$. He does not state the exact temperature to which this applies, but all his experiments seem always to have been made between 10ᵁ and 13°, so that we may assume 11°·5 to be the mean temperature of his experiments. Rowland's value at that temperature is $4 \cdot 1999 \times 10^7$ *. We must draw attention to one point in Miculescu's work which requires clearing up before we can give to it any decisive value. Everything in the experiments depends on the measurement of a couple, the arm of the couple being the distance between two knife-edges ; one of them had to support a weight of more than 43 kilograms. The distance between these knife-edges is said to have been 28 cms. in all experiments. Very insufficient information is given, however, as to how that distance was measured, and it would almost seem as if the author had trusted to the maker in adjusting the central knife-edge to the zero-point of that scale. If the apparatus is still in existence, it might be well to make sure that no error has been introduced through a wrong estimate of the distance of the lever-arm."

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* I do not agree with Professor Schuster's interpretation of Rowland's value at this temperature. The curve on Plate VII. is constructed from the values given by Rowland in his final table (p. 196), and 4·197 would appear to be the more accurate value.

DIETERICI.—These experiments are characteristic examples of the care and accuracy by which Dieterici's work is distinguished, and possess one great feature of excellence, *i. e.* their results are much less dependent than in previous cases on the thermometers used by the observer, since no change of temperature takes place during an experiment. One correction, however, is necessary in his value of J (4·2436 × 10⁷). The resistance of his conductor was measured in terms of a legal ohm, and the correction to the Board of Trade or "true ohm" reduces this value to 4·233 × 10⁷, expressed in terms of the mean calorie. It must be remembered, however, that Bunsen, Schüller and Wartha, and Velten differ by 1 part in 250 regarding the value of a constant on which the numerical value obtained by Dieterici is dependent.

MY OWN EXPERIMENTS.—Naturally I can here say but little regarding my own work. I would, however, venture to point out in what I consider the strength of that determination lies. Two entirely different systems of thermometry were used, viz.: a platinum-thermometer scale (the reduction to the air-thermometer being based on the previous observations by Professor Callendar and myself); also the thermometers thus standardized were compared, *under the conditions in which they were used*, with the nitrogen-scale of the Bureau International, when the range-value was found to be practically identical and the actual elevation, as determined by the two methods, differed only by 0°·005. When it is remembered how extremely dissimilar were the two methods of standardization, the close agreement between the results greatly strengthens the conclusions. Again, the nature of the experiments enabled me to vary the conditions to a greater extent than was found possible by other observers, and thus any constant errors would probably have been detected. That this was the case was shown by the persistent failures (during the years 1888 to 1891) to obtain consistent results when the conditions were thus altered. The weakness of those experiments was that small masses of water were used. These masses were, however, chosen deliberately, as any increase would have led to the accumulation of other causes of error *. The value resulting from these experiments was given as 4·198 in terms of a thermal unit at 15° C.† Professor Schuster has since pointed out a necessary correction of 1 in 4000 due to the specific heat of the air displaced by the water. This would give 4·199 × 10⁷. In my original paper Mr. Clark and I stated our impression that in assuming the mean E.M.F. of our cells as 1·4344, instead of 1·4342, we were possibly in error, as there

* Trans. Roy. Soc. vol. clxxxiv. A. p. 415.
† Proc. Roy. Soc., January 1894.

were reasons for suspecting that the temperature of the Cavendish Standard, at the time of comparison, slightly exceeded that of our cells.

In 'Science Progress,' April 1894, I entered fully into this matter, and a recomparison with the Cavendish Standard made during the spring of this year (when greater attention was paid to securing the equality of the temperature) confirms my opinion that 1·4342 was the more probable mean value of my Clark's cells. This would diminish the value of J by 1 in 4000, and it would thus remain $4·198 \times 10^7$ *.

SCHUSTER AND GANNON.—I regret that at the time of writing I have only been able to obtain an abstract of the important investigation by Professor Schuster and Mr. Gannon. This abstract, however, is sufficient to indicate the value of

* There is one criticism of Professor Schuster and Mr. Gannon's regarding my work to which I am glad to have this opportunity of replying. The following is a quotation from the Abstract of their paper:—" We may reasonably estimate the uncertainty due to the cooling correction by calculating what the observed rate of cooling, either at the beginning or the end of the experiment, must have been in order to produce a difference of one part in a thousand in the final results." They remark later:—" In the experiments quoted by Mr. Griffiths at p. 482, the loss of heat due to radiation and conduction at the end of his experiments amounts to about 9 per cent. of his heat-supply. If such loss had been wrongly estimated to 1 per cent. an error of one-tenth per cent. would result in the final value." This criticism may be just when the rate of rise at the exterior temperature is determined by the time of rising over the *whole range*, as was the case in Professor Schuster and Mr. Gannon's experiments; in my own, however, the rising rate at each part of the range was determined by separate and independent observations. If their criticism were sound, the uncertainty as to the rate of rise at any given temperature would depend on the temperature-range of the experiments, whereas, had I doubled the ranges my conclusions as to the value of $\frac{d\theta}{dt}$, when the temperature of the calorimeter crossed the exterior temperature, would remain unchanged. True, the rate of change in the heat-capacity of water would be affected by errors in the cooling-rate at the extremities of the range, but my resulting value of J would remain unaltered when expressed in terms of the heat-capacity of water at the exterior temperature.

I think, therefore, that Professor Schuster and Mr. Gannon overestimate the possible errors in my results due to errors in the determination of the "cooling rate." With regard to this "cooling correction" I am in agreement with their conclusion that it probably varies with the rate of rise, and I had, before the publication of Professor Schuster and Mr. Gannon's work, expressed my views on this point in a paper on the "Specific Heat of Aniline" communicated to this Section in 1894 [1]. I have there shown that ρ (the "cooling coefficient") is a function of the rate of rise in temperature, and I described some experiments which led to the conclusion that the error, under circumstances similar to those prevailing in my J experiments, was of small importance unless the variations in the rate of rise were extreme.

[1] See also Phil. Mag., January 1895.

their work. It is unnecessary to say that in this case there is not the usual doubt as to the thermometric data. In the absence of further details I feel that it would be unbecoming on my part to venture on a criticism of the experimental methods. The result is $4 \cdot 1905 \times 10^7$ ergs, expressed in terms of " a thermal unit at $19° \cdot 1$."

In endeavouring to make a comparison of the above results the usual difficulty presents itself, viz., the impossibility of expressing them with certainty in terms of any common thermal unit. This does not apply to Rowland's determinations or to my own, since the observations extended over temperature-ranges of $5°$ to $34°$ and $14°$ to $26°$ respectively ; whereas the other observers contented themselves with observations grouped closely about some particular temperature. Fortunately, with the exception of Dieterici's, the difference between the mean temperatures is comparatively small, extending from $11° \cdot 5$ in the case of Miculescu to $19° \cdot 1$ in the case of Schuster and Gannon. For the reduction of the observations of Miculescu, Joule, and Schuster and Gannon to some common standard, I propose to take the mean of the conclusions of Rowland, Bartoli and Stracciati, and my own as to the changes in the specific heat of water over the range $15°$ to $20°$, and the mean of Rowland and Bartoli and Stracciati over the range $10°$ to $15°$, as mine do not extend much below the latter temperature. The results may be expressed as follows :—

Range $10°$ to $15°$. Coefficient $\cdot 000414$.
 ,, $15°$,, $20°$. ,, $\cdot 000284$ *.

If, instead of taking the mean of the results of the above observers over these ranges, we adopted the conclusions of any one of them, it would not affect the values of J at $15°$ in any of the selected cases by more than 1 in 2000.

The results are shown in the following Table :—

Values of J expressed in terms of " a thermal unit at $15°$ C."

Griffiths	$4 \cdot 198 \times 10^7$	ergs.
Schuster and Gannon . .	$4 \cdot 195 \times 10^7$	,,
Rowland	$4 \cdot 189 \times 10^7$	,,
Joule's later exps. (R)† .	$4 \cdot 182 \times 10^7$	,,
Miculescu	$4 \cdot 181 \times 10^7$	,,
Joule's later exps. (S)‡ .	$4 \cdot 174 \times 10^7$	,,

* This mean closely approximates to my own coefficient, viz. $\cdot 000266$.
† In terms of Rowland's air-thermometer.
‡ Value resulting from Professor Schuster's determination of the scale-value of Joule's thermometers in terms of the Nitrogen Thermometer of the Bureau International (Phil. Mag. June 1895).

In addition to the above we have Dieterici's value after correction to the "true ohm," viz. 4·233 in terms of the "mean calorie." No purpose would be gained by endeavouring to express Dieterici's results in terms of the same unit as the others, for, as I have endeavoured to show, the evidence regarding the relation between the "mean calorie" and the "thermal unit at 15°" is unfortunately so contradictory that no comparison is possible until further light is thrown on the subject.

Plate VII. shows, more clearly than the table, the relation between the different determinations. The dotted lines indicate the values deduced by the above assumptions with regard to the changes in the specific heat of water.

I quite agree with Professor Schuster's conclusion* that greater value should be attached to results based on mechanical rather than on electrical methods. He thinks it probable that the correct value lies somewhere between Joule and Rowland. When we remember, however, the very small rises of temperature on which the conclusions of Joule are based, and the inevitable uncertainty connected with the re-standardization of his thermometers after so great a lapse of time, we should, I think, give far the greater weight to Rowland's conclusions.

Many arguments can be adduced in support of the electrical method of investigation. The experimental difficulties are less than when other methods are adopted, but on the other hand the results are dependent on the validity of our values of the electrical units. I felt this so strongly that I endeavoured so to phrase the title of my own paper on this subject as to show that I regarded that work as an effort to "establish the relation between the electrical and mechanical units," and to trace the "changes in the capacity for heat of water," rather than as a direct determination of J. I trust that I shall not be considered too presumptuous if I state that some doubts exist in my own mind as to the absolute accuracy of the electro-chemical equivalent of silver. A change of 1 in 1000 in that constant would bring into very close approximation the results obtained by Schuster and Gannon, Rowland, and myself; for, as a consequence, the number representing the electromotive force of a Clark's cell would be also changed. No such alteration, however, could make the agreement absolute owing to the different rate of change with temperature indicated by the experiments by Rowland and myself; our differences, therefore, must be partially due to thermometry, for no alteration in the constants involved in the work of

* Phil. Mag., June 1895, p. 501.

either observer could secure identity at more than one temperature.

An inspection of Plate VII. at temperature 10° will show that the agreement between the values of Rowland, Schuster and Gannon *, and my own is there very close. Rowland's result at that temperature is $4 \cdot 2 \times 10^7$, and if we assume that value at 10° it is probable that our error will be of small dimensions.

Part III.

Practical Suggestions.

The ideal thermal unit should

- (A) be a natural, not an arbitrary, one, and have some real relation with other units of energy.

  (In absence of further reasons the educational value of such a relation is sufficient to establish this proposition.)

- (B) It should not be dependent on the observations or conclusions of any one investigator. Any such dependence must certainly result in future corrections and changes.

- (C) It should be of a convenient magnitude, and should cause as little disturbance as possible in the numerical values resulting from our present system of thermal measurements.

We cannot, I think, do better in this matter than follow the principles which have governed the choice of our electrical units. Let us consider for a moment the steps by which we have arrived at our present value of the ohm. The value of the ideal unit was first defined, that value being some convenient multiple of an absolute unit. The first attempt at the practical standard, whose resistance should be that of the ideal one, is that of the B. A. Committee of 1863, and, as is well-known, their conclusion, expressed in terms of the length of a column of mercury a square millim. in section at temperature 0°, was
$$104 \cdot 83 \text{ centim.}$$

The work of Rayleigh and Schuster, Rowland, Glazebrook, and others clearly demonstrated the existence of error, which led to a redetermination by the International Congress of 1881, when the value was increased to
$$106 \cdot 0 \text{ centim.}$$

Lastly, we have the (so-called) final determination of the

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* Assuming the validity of the reduction to 10° C.

Electrical Standards committee appointed by the Board of Trade (July 1891), when the length was increased to

106·3 centim.

I have recalled these familiar facts in order to show how great has been the advantage of proceeding on a sound theoretical basis. We have here a change in the practical standard amounting to $1\frac{1}{2}$ per cent., but the disturbance caused by the successive corrections has been small, for the fundamental basis of the whole system has remained unchanged. Had the unit of resistance been arbitrarily selected and dependent on the behaviour of some particular conductor, which further was subject to changes with whose nature we were but dimly acquainted, each successive alteration would have damaged the whole superstructure, and the progress of electrical science would have been hampered and retarded. Why not proceed in an analogous manner with regard to a system of thermal measurements? viz., first define an ideal unit based on a system of absolute measurements and of a convenient magnitude for practical use, bearing in mind conditions (A) and (C) *supra*.

Let us next apply the information we already possess for the purpose of making a first approximation to the physical measurement of the unit thus selected, and, to use the words of Professor Callendar, " leave it to a more enlightened and skilful generation "[*] to make a second, and if necessary (as in the case of the ohm) a third approximation.

It would, I think, be advisable to give the ideal thermodynamic unit some distinctive title. Unfortunately the most appropriate one (a Joule) has already been annexed[†], and such being the case the ideal unit might with great propriety be termed a " ROWLAND " [‡], at all events I propose to make a temporary use of the name in that sense.

I employ the name " THERM " to indicate " the quantity of heat required to raise 1 grm. of water (measured *in vacuo*) through 1° C. of the nitrogen-thermometer of the Bureau International at a temperature of $t°$ C. by that thermometer." Thus the value of a THERM would be a function of the temperature.

The " ROWLAND " should be of such a magnitude that a THERM at some convenient temperature (say within the range 10° to 20° C.) would be its heat equivalent. The particular

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[*] Phil. Trans. 1887, A, p. 195.

[†] A Joule $= 10^7$ ergs.

[‡] The names " MEYER " and " KELVIN " also naturally suggest themselves as both appropriate and convenient.

THERM, which is the exact equivalent of a "ROWLAND," could be denoted by the phrase STANDARD THERM.

Adopting the system of nomenclature above indicated I venture to bring forward the following propositions for the consideration of the Committee:—

(I.) That 42×10^6 ergs be termed a "ROWLAND."

(II.) That (pending the results of further investigations) we assume that a THERM at $10°$ is a STANDARD THERM, *i. e.* the equivalent of a "ROWLAND."

(III.) In order to enable observers to express their results in terms of a STANDARD THERM, we (pending the results of further investigations) assume the validity of the following expressions over the temperature ranges indicated:—

Range $10°$ to $15°$,

$$Q_{10} = Q_t \{1 - ·000415\,(t-10)\}^*;$$

and over the range $15°$ to $20°$,

$$Q_{10} = Q_t \{·99935 - ·000284\,(t-10)\}\dagger.$$

If this last suggestion was generally adopted we should be able, when our knowledge of these changes became more exact, to make the necessary corrections in the results of observations which had been reduced by these formulæ.

I have suggested the value 42×10^6, since it is obviously convenient to have as simple a number as possible, and the adoption of this value would cause but little dislocation in our existing system of measurements. True, this entails the adoption of the somewhat low temperature $10°$ for the STANDARD THERM, but in order to secure a more convenient temperature, say $15°$, it would be necessary to replace 42 by 41·89—a somewhat less convenient number. Further, the close correspondence previously referred to between several observers at $10°$ is an additional argument in favour of the selection of the value above suggested.

Of course propositions (II.) and (III.) would undergo alteration as our knowledge became more accurate; the *exact* temperature at which a THERM may be regarded as the STANDARD THERM being ascertained by successive approximations.

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* The mean of the conclusions of Rowland and Bartoli and Stracciati over this range.

† The mean of the observations of Rowland, Bartoli and Stracciati, and Griffiths over the range 15^c to $20°$, the reduction from $15°$ to $10°$ being made by the preceding expression.

If it be thought that the advantage of adopting what I believe is termed a "round number" as a multiple of the absolute unit is more than counterbalanced by the selection of so low a temperature as one near 10° for the STANDARD THERM, I would suggest the following alternative proposals:—

(I.) That $41{\cdot}89 \times 10^6$ ergs be termed a "ROWLAND."

(II.) That (pending the results of further investigations) we assume that a therm at 15° is a STANDARD THERM.

(III.) In order to enable observers to express their results in terms of a STANDARD THERM, we (pending the results of further investigations) assume the validity of the following expressions over the temperature ranges indicated:—

Range 10° to 15°,
$$Q_{15} = \tilde{Q}_t \{1 + {\cdot}000414(15 - t)\};$$

Range 15° to 20°,
$$Q_{15} = Q_t \{1 - {\cdot}000284(t - 15)\}.$$

I think it improbable that the error introduced by proposition II. exceeds 1 in 800 in either case; at all events I believe it to be as close an approximation as the present state of our knowledge permits.

An inspection of Plate VII. will show that the actual mean of *all* the selected observers at 10° and at 15° is as follows:—

	At 10°.	At 15°.
Assuming Joule (R)*	$(41{\cdot}971 \pm {\cdot}023) \times 10^6$;	$(41{\cdot}891 \pm {\cdot}023) \times 10^6$
,, Joule (S)*	$(41{\cdot}958 \pm {\cdot}029) \times 10^6$;	$(41{\cdot}875 \pm {\cdot}029) \times 10^6$

but I repeat that greater importance should be attached to the results of Rowland's experiments than to those of other observers. Hence I selected 42 at 10° and 41·89 at 15° as the most probable values.

With regard to proposition (III.) our position is more uncertain, but when we remember the entirely dissimilar method of experiment adopted by the observers upon whose results these formulæ are based, the comparatively close agreement over these ranges carries weight.

Another subject to which the attention of the Committee should be directed is the determination of the relation between the mean calorie and the STANDARD THERM, suggested in proposition (II.). Until this is accomplished we shall be unable

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* See note, p. 448, *ante.*

to utilize the observations which are based on the use of
Bunsen's calorimeter (such as Dieterici's, *supra*), a method of
extreme value when we remember that the conclusions are
practically independent of thermometry.

I have brought this matter before your notice at the request
of the Officers of this Section, and, while sensible of the honour
thus conferred upon me, I regret that they did not entrust so
important a task to more able and influential hands.   At the
same time I hope that a consideration of the facts and argu-
ments brought forward may stimulate discussion, and thus
accelerate our progress on to firmer ground.

Further individual effort will avail but little ; what is
necessary is the decision of some body having authority, whose
conclusions will command the respect and assent of the
scientific world.

XXXIX. *On the Pressures of Saturation of Oxygen.*
By Thaddeus Estreicher *.

ON account of the present tendency of science to undertake
different kinds of researches at very low temperatures,
liquid oxygen is every day more widely employed in labora-
tories : it gives us, it is true, temperatures a little higher
than liquefied air or nitrogen, but it has this advantage over
air, that its temperature is in exact relation with its pressure,
not being a mixture of gases ; and over nitrogen, that it does
not become solid even under the lowest pressures : it is there-
fore the best cooling agent.

Accordingly, besides its theoretical importance, the deter-
mination of the pressures of oxygen under pressures lower than
one atmosphere has also a practical interest ; for if we draw
a suitable curve, we can directly read the temperature from it,
knowing the pressure under which the oxygen is boiling.
With a similar purpose, Prof. Olszewski has determined a
series of temperatures and corresponding pressures below one
atmosphere for ethylene †.

The late Prof. Wróblewski has already made such mea-
surements for oxygen ‡.   He determined the temperatures
for pressures between 160 and 20 millim., leaving the
temperatures corresponding to the pressures above 160 and

below 20 millim. undetermined. Besides, the points of his curve are often rather far from their places on the ideal line. Finally, Wróblewski started with the assumption that the hydrogen-thermometer gives too low results at temperatures lower than −193°, and used a thermoelectric junction to measure such temperatures ; in consequence of which, for instance, the temperature −207°·2 of the hydrogen-thermometer was only −200°·4 according to the thermoelectric junction ; these differences changed irregularly with the temperature. The measurements by means of a hydrogen-thermometer have not yet been systematically carried out.

We have no reason to suppose that the hydrogen-thermometer fails at very low temperatures [*] ; Prof. Olszewski's experiments with thermometers filled with nitrogen, oxygen, and nitric oxide [†], as well as Dr. P. Chappuis's with a carbon-dioxide thermometer [‡], showed that gas-thermometers give temperatures in agreement with true data, even at temperatures which are much lower than the critical temperature of the corresponding gas. Moreover a comparison of the hydrogen-thermometer with an electric thermometer based on an increase of electrical conductivity when the temperature is diminished, shows that both are pretty well in agreement ; the line representing the variation of electrical resistance with the variation of temperature is nearly straight [§]. If we use Wróblewski's determinations (taking his results to − 193° to be in agreement with the hydrogen-thermometer) to draw the line of resistances, on approaching −200° we see an inflection of the line down towards the axis of temperatures, contrary to its whole course as far as this temperature.

If we draw by means of the numbers given by Wróblewski the curve of the boiling-points of oxygen, and compare it with the curve we have obtained from measurements with a hydrogen-thermometer, we at once see the very irregular shape of his line, and the disagreement of temperatures. The temperatures which he assumed to be in agreement with the hydrogen-temperatures to −193° are even at the temperature of −190°·5 (corresponding to the pressure of 90 millim.) lower by 8° than those of the hydrogen-thermometer. This

[*] Witkowski, *Rozprawy* (Transactions) of the Crac. Acad. [2] iii. p. 380 (1891).

[†] Transact. of the Crac. Acad. xiv. p. 283. Also Wied. *Ann.* xxxi. p. 69 (1887).

[‡] Tiav. et Mém. du Bureau Intern. d. Poids et Mesures, vi. pp. 92–104 (1888).

[§] *Cf.* Dewar and Fleming, 'On the Electr. Resist. etc.,' Phil. Mag. [5] xxxvi. p. 271 (1893).

difference afterwards decreases, and amounts to 7° at the thermoelectrical temperature −200°·4 ; Wróblewski did not go further.   Besides this irregularity, Dr. Ch.-Ed. Guillaume * proved that we have no reason to distrust the hydrogen-thermometer at the lowest temperatures hitherto reached, and that if we were obliged to extrapolate temperatures, it would be better to do so by measurements of the variation of resistance rather than by the electromotive force of the contact ; that the formula by means of which Wróblewski calculated the temperatures was badly deduced, and, as a necessary sequence, that his results do not agree with fact.

For these reasons, Prof. Olszewski directed me to measure the temperatures of saturated vapour of oxygen by means of a hydrogen-thermometer.   In the present state of our knowledge we might hope to obtain more positive results, were it but for this reason, that the manipulation of liquefied gases in quantities incomparably larger and under conditions much more convenient than was possible a few years ago, now presents neither great difficulties nor dangers in practice.

Oxygen was liquefied in the apparatus of Prof. Olszewski's construction †, which served to obtain large quantities of liquefied gases under atmospheric pressure.   From the steel cylinder, in which oxygen was liquefied, it was poured out into the glass vessel *a*, surrounded by three others in order to isolate liquid oxygen from the influence of external heat, and to prevent the vessel from freezing on the outside, which would render it impossible to observe the liquid oxygen within ; for the same reason there was at the bottom of the outermost vessel *b* a layer of phosphoric anhydride.   The second vessel had a brass setting above, to which a cover *c*, also of brass, to be fixed on it by means of four screws *s s′*, was closely adapted.   In this cover, four openings were made : the central one, which was the largest, was destined to receive a little hydrogen-thermometer *t* ; round about it were three openings : the first served to let in a narrow glass tube *h*, admitting a very slow stream of hydrogen, which was used to aid the oxygen in boiling when the pressure was very much reduced.   Through the second the copper tube *o* passed from the liquefying apparatus ; this tube, closed at the end, had four lateral openings nearly at the end, in order to prevent the liquid from being thrown out of the vessel ; but to prevent liquid oxygen from

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* *Archives d. Sc. Phys. et Natur.* 1888 ; afterwards *L'Industrie Électr.* i. p. 77.

† Transactions of the Crac. Acad. [2] iii. p. 385 ; *Bullet. Intern.* 1890, p. 177.   Also Phil. Mag. [5] xxxix. p. 193.

pouring against the sides in a strong jet and consequently evaporating too rapidly, a short thin-walled glass tube *z* surrounding the copper tube served to collect and to direct downwards all the four streams of oxygen. In the third opening
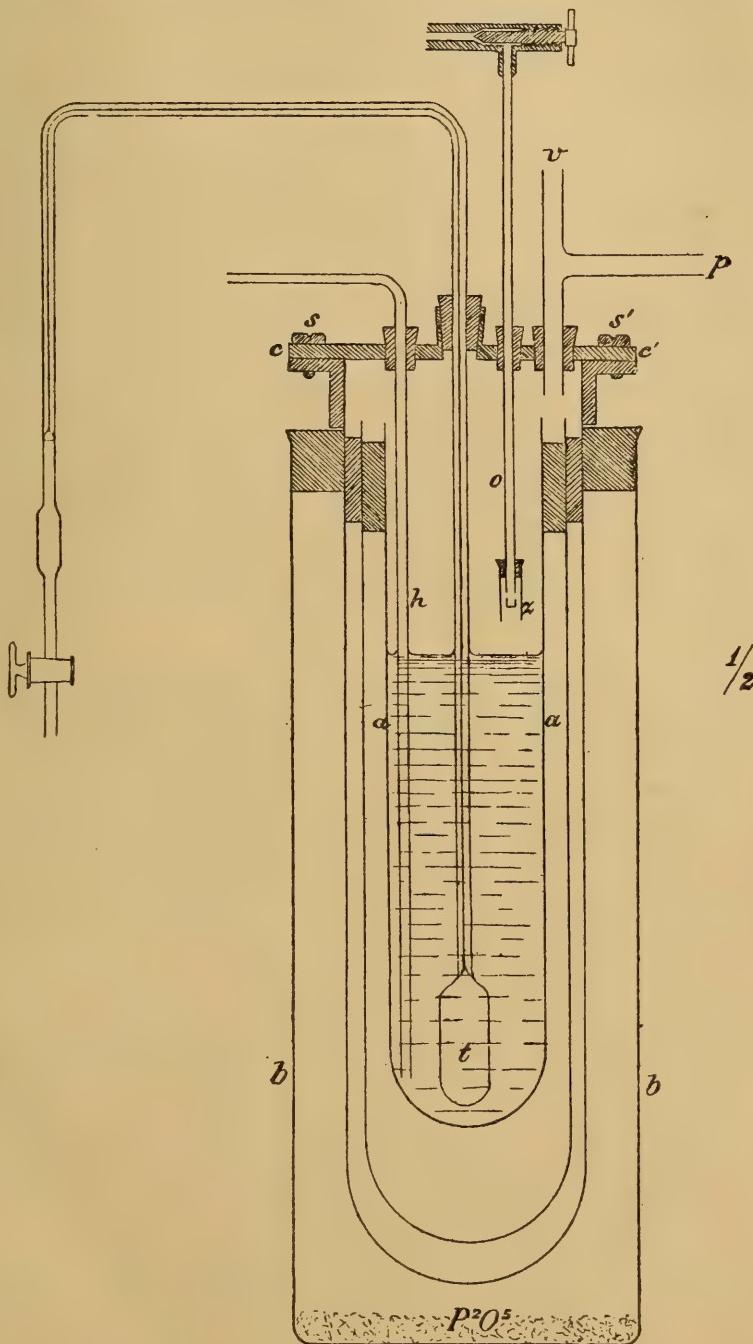
was placed a T-shaped glass tube connected at one end *p* with a large Burckhardt air-pump, worked by means of a gas-

engine, at the other end *v* with vacuometers, so that it was possible at any time to read the pressure the liquid was under. Between this apparatus and the air-pump there was placed a screw-cock, so that by turning it more or less it was possible to regulate very precisely the pressure of the oxygen, and to keep up at will and for a long time the pressure we required.

As Prof. Olszewski pointed out some years ago, liquid oxygen can be preserved for a long time under the usual pressure[*]; when the vessel described is employed, liquid oxygen may be preserved for hours ; the triple air-layer and the quadruple glass walls isolate it perfectly well from the influence of external heat.   By pumping in order to lower the temperature, we obtain round the liquid oxygen a vacuum, by which a vessel of the sort approaches the principle of the " vacuum-jacketed vessels " of Prof. Dewar.   Whether such a vessel is in practice better than one surrounded by three layers of dry air, seems to me not certain ; at all events, the deposit of mercury, fixed on the walls in the vacuum to prevent the action of the radiant heat, besides destroying transparency, is of no use, as follows from M. Pictet's researches [†].   Such vessels as I have described have been employed for several years in Prof. Olszewski's laboratory, and have proved very useful.

I have performed three series of experiments ; several (generally three) determinations of the state of the thermometer corresponded to each pressure ; the mean temperature thus determined was considered as corresponding to the pressure examined.   The curves traced according to these data are generally in close agreement, especially in their lower course ; at higher pressures there is a slight difference, but never more than $0°\cdot6$.

First Series.

No.	Pressure.	Temperature.	No.	Pressure.	Temperature.
	millim.	°		millim.	°
1......	735·9	−182·7	6......	11·0	−209·7
2......	533·9	−185·1	7......	10·0	−210·2
3......	433·9	−187·1	8......	9·0	−211·4
4......	333·9	−189·4	9......	8·0	−211·2
5......	233·9	−192·1			

The slight disagreement between the two last determinations

[*] *Bullet. Intern.* of the Crac. Acad. January 1891, p. 45; also Wied. *Ann.* xlii. p. 664.

[†] *Zeitschr. f. physik. Chemie,* xvi. p. 417 (1895).

is to be ascribed to the influence of the hydrogen, which is passed through the liquid oxygen in a slow current ; when we employ such low pressures the boiling must be facilitated by this means.

Second Series.

No.	Pressure.	Temperature.	No.	Pressure.	Temperature.
	millim.	°		millim.	°
1......	731·1	−182·2	8 ...	54·1	−201·6
2......	629·1	−183·3	9 ...	37·5	−204·9
3......	479·1	−185·8	10 ...	33·5	−205·2
4......	279·1	−190·5	11 ...	16·0	−208·8
5......	179·1	−194·0	12 ...	16·0	−209·3
6......	129·1	−196·25	13 ...	15·0	−209·7
7......	79·1	−199·5	14 ...	13·0	−210·2

Third Series.

No.	Pressure.	Temperature.	No.	Pressure.	Temperature.
	millim.	°		millim.	°
1 ...	743·8	−182·56*	12 ...	11·5	−209·5
2 ...	141·8	−195·9	13 ...	11·0	−209·7
3 ...	91·8	−198·7	14 ...	10·5	−209·8
4 ...	61·8	--201·1	15 ...	9·5	−210·2
5 ...	41·8	−203·4	16 ...	9·0	−210·4
6 ...	31·8	−204·8	17 ...	8·75	−210·6
7 ...	21·8	−206·8	18 ...	8·5	−210·8
8 ...	14·5	−208·6	19 ...	8·0	−211·1
9 ...	13·0	−208·9	20 ...	7·75	−211·2
10 ...	12·5	−209·2	21 ...	7·5	−211·2
11 ...	12·0	−209·3			

* This is the mean of 22 determinations.

All the temperatures have been calculated to two decimal places ; the second decimal served only for correction.

Having thus determined the pressures of saturation for oxygen, I wished to ascertain if the rule of van der Waals * applied to this body. This law says :—" If the absolute temperatures of various substances are proportional to their absolute critical temperatures, their vapour-pressures will be proportional to their critical pressures." This statement has been tried for different substances, but " has not been proved by experiment to be true, except in a very limited number of cases" †. I therefore divided my numbers by the critical constants, and compared the results with the numbers for several other bodies, drawing by means of these numbers the

* Van der Waals, *Continuität*, transl. by Roth, 1881, p. 128.
† Young, 'On the Generalizations.....' Phil. Mag. [5] xxxiii. p. 173, 1892.

"reduced curves." It appears that these curves are not identical, and the differences between them are too great to be explained by errors of observation. The reason lies elsewhere, namely, in the disagreement of the quantity f for different bodies. From Prof. Guye's paper [*], we know that f in van der Waals's formula

$$-\log \pi = f\frac{1-\tau}{\tau},$$

in which π and τ are reduced pressure and temperature $\left(\frac{p}{p_c} \text{ and } \frac{T}{T_c}\right)$, is not constant, but differs for different substances, and that its value is generally about 3·06, except for associating substances, which have more complex molecules in the liquid than in the gaseous state ; for then f is higher than 3·06, and may even be higher than 4. In his first paper quoted above, Prof. Guye proves that the curve of pressures of saturation for associating liquids intersects the curves for non-associating bodies (*l. c.* p. 168). Thence we can easily infer that such a curve, when reduced, is farther from the axis of pressures and nearer the axis of temperatures than a curve for a normal body. And, indeed, the curves for oxygen, carbon bisulphide, ethylene, and other non-associating bodies lie much nearer the axis of π than the curves for water, acetic acid, and alcohols, which bodies are associated, according to Messrs. Ramsay and Shields [†]. It follows thence that the value of f for associating bodies must differ and be greater than the normal value. For, from the formula of Prof. van der Waals,

$$-\log \pi = f\frac{1-\tau}{\tau}, \quad \text{and} \quad -\log \pi' = f'\frac{1-\tau'}{\tau'}, \quad \cdot \quad (1)$$

for another body we have at corresponding temperatures,

$$\frac{f}{f'} = \frac{\log \pi}{\log \pi'}. \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (2)$$

Similarly, at corresponding pressures,

$$\frac{f}{f'} = \frac{1-\tau'}{1-\tau} \cdot \frac{\tau}{\tau'}. \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (3)$$

But as, for associating substances, π is smaller at corre-

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[*] *Archives d. Sc. phys. et natur. d. Genève*, xxxi. pp. 163 and 463. Also Prof. Ramsay, Proc. R. S. April 26, 1894.

[†] Phil. Trans. clxxxiv. A. p. 167. Also *Zeitschr. f. physik. Chemie*, xii. p. 433.

sponding temperatures than for such as are non-associating, we can deduce from (2) that f for the first-named bodies must be greater than its normal value. Similarly with equation (3).

In the following tables I give the values of f for different bodies in the column of pressures corresponding to pressures of oxygen lower than one atmosphere, then at low pressures; the ratios of absolute temperatures at corresponding pressures to the absolute critical temperatures of six of these bodies (viz., fluorbenzene, ether, acetic acid, and the three first alcohols) are calculated and published by Prof. S. Young*, wherefrom it can be seen that these substances do not really agree as regards the reduced curves.

Oxygen.   (Crit. const. of Olszewski.)

No.	Temperature.	$f.$	No.	Temperature.	$f.$
1......	$-210\overset{\circ}{\cdot}6$	2·477	8 ...	$-198\overset{\circ}{\cdot}7$	2·440
2......	$-209\cdot8$	2·476	9 ...	$-196\cdot25$	2·454
3......	$-208\cdot9$	2·471	10 ...	$-194\cdot0$	2·451
4......	$-206\cdot8$	2·445	11 ...	$-190\cdot5$	2·463
5......	$-204\cdot8$	2·446	12 ...	$-185\cdot8$	2·481
6......	$-203\cdot4$	2·440	13 ...	$-183\cdot3$	2·488
7......	$-201\cdot1$	2·442	14 ...	$-182\cdot2$	2·467

Ethylene.   (Crit. const. and vapour-pressures of Olszewski.)

No.	Temperature.	$f.$	No.	Temperature.	$f.$
1......	$-150\overset{\circ}{\cdot}4$	2·752	7 ...	$-122\overset{\circ}{\cdot}0$	2·778
2......	$-148\cdot0$	2·787	8 ...	$-115\cdot5$	2·763
3......	$-139\cdot0$	2·788	9 ...	$-111\cdot0$	2·749
4......	$-132\cdot0$	2·824	10 ...	$-108\cdot0$	2·724
5......	$-129\cdot7$	2·806	11 ...	$-105\cdot0$	2·710
6......	$-126\cdot0$	2·777			

Water.   (Crit. const. of Battelli, vap.-pres. of Zeuner.)

No.	Temperature.	$f.$	No.	Temperature.	$f.$
1......	$+30\overset{\circ}{}$	3·328	8 ...	$+\ 75$	3·260
2......	$+35$	3·319	9 ...	$+\ 85$	3·248
3......	$+40$	3·311	10 ...	$+\ 95$	3·236
4......	$+45$	3·303	11 ...	$+105$	3·226
5......	$+50$	3·298	12 ...	$+115$	3·216
6......	$+55$	3·287	13 ...	$+125$	3·208
7......	$+65$	3·273	14 ...	$+135$	3·200

* Phil. Mag. [5] xxxvii. p. 3 (1894).

Values for f for :

Temp.	CS₂.	C₆H₅F.	(C₂H₅)₂O.	CH₃.COOH.	CH₃OH.	C₂H₅OH.	n-C₃H₇OH.	i-C₄H₉OH.
− 20	2·650	......	3·107					
− 10	2·703	3·074	3·067		3·837	4·014		
0	2·636	3·067	3·041		3·808	4·009		
+ 10	2·631	3·042	3·020	3·467	3·785	3·994		
20	2·630	3·026	3·001	3·456	3·767	3·975	4·087	
30	2·624	3·011	......	3·441	3·756	3·952	4·036	4·293
40	2·622	2·994	......	3·430	3·744	3·928	3·988	4·263
50	2·621	2·979	......	3·420	3·731	3·902	3·942	4·229
60	......	2·965	......		3·724	3·876	3·899	4·212
70	......	2·952	......	3·413	3·719	3·849	3·860	4·159
80	......	2·940	......	3·406	3·646	3·821	3·825	4·127
90	......	......	......	3·400	......	......	3·795	4·098
100	......	......	......	3·396	......	......	3·772	4·072
110	......	......	......	3·387	......	......	......	4·047
120	......	......	......	3·387	......	......		
	Crit. const. Battelli ; vapour-tens. Regnault.	Crit. const. and vap.-tens. Young.	C. c. and v.-p., Ramsay and Young.	C. c. and v.-p., Ramsay and Young.	C. c. Ramsay and Young ; v.-p. Regnault.	C. c. Ramsay and Young ; v.-p. Regnault.	C. c. Ramsay and Young ; v.-p. Schmidt.	C. c. Nadejdine ; v.-p. Schmidt.

From the foregoing numbers we see that the value of f always decreases with increase of temperature, both for associating and non-associating bodies. The only exception is the value of f for carbon bisulphide at $-10°$. The oscillations of f for oxygen and ethylene are simply due to difficulties in executing the experiments at such low temperatures. The difference between the highest and the lowest value for oxygen is, however, not so great—it does not reach 2 per cent. ; whilst the mean values for ether, from Prof. Battelli's and Profs. Ramsay and Young's determinations, differ by 3·3 per cent.*

From the numbers above and the equations (2) and (3) it follows that the disagreement of f with its normal value is a measure of the disagreement of specific pressures π at corresponding temperatures, and *vice versâ.* The association of the molecules of the liquid has an influence on f, but is not the only reason of its increasing. In such a case f would, for instance, become smaller with the increase of the molecular weight in the series of alcohols, for Messrs. Ramsay and Shields have proved that the association decreases with the increase of the molecular weight. Besides, of ten esters for which Prof. Guye has calculated f, six have f much higher than 3·06, so that they would appear to be associated ; from the paper of Messrs. Ramsay and Shields it follows that they are not associated. That shows that the association, but not it *alone,* exerts an influence on f. It would therefore be necessary to find out the relation between f and the nature of the substance ; perhaps there is some relation with the molecular weight, for we see that the heaviest of the alcohols examined, isobutyl alcohol, has the highest f; but to get more knowledge on this point we shall have to obtain more information on the critical constants and vapour-pressures of different bodies, those of homologous chemical structure being best for the purpose.

XL. *On a Simple Geometrical Construction for finding the Intensity of Illumination at any Point of a Plane due to a Small Source of Light symmetrical about an Axis perpendicular to that Plane.* By CHARLES H. LEES, *D.Sc.*†

THE following geometrical construction for finding the illumination of a plane due to a given source of light of

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* *Cf.* Guye, *Arch. d. Sc. ph. et nat. Genève,* xxxi. p. 471.
† Communicated by the Author.

small area, as, for example, an Argand gas-flame or an arc-light, symmetrical about an axis perpendicular to the plane, will, I trust, be found simpler to understand and easier to carry out in practice than that proposed by Loppe, and quoted by Palaz, in his *Photométrie Industrielle*, p. 253.

The source of light is supposed to be at a distance from walls &c. producing diffuse reflexion, but it may be provided itself with reflectors, if the photometer-curves for the source are taken with the reflectors in position. The most important cases in practice are those in which the illuminated plane is horizontal—in general the ground ; and the source of light is symmetrical about a vertical axis.

Let A, B, C, D be the photometer-curve of the given source of light at L, the distances L A and L B &c. being equal, on some convenient scale indicated by the figures 15 or 700 on the circles, to the intensity of light sent out by the source in the directions L A, L B, &c.

Fig. 1.
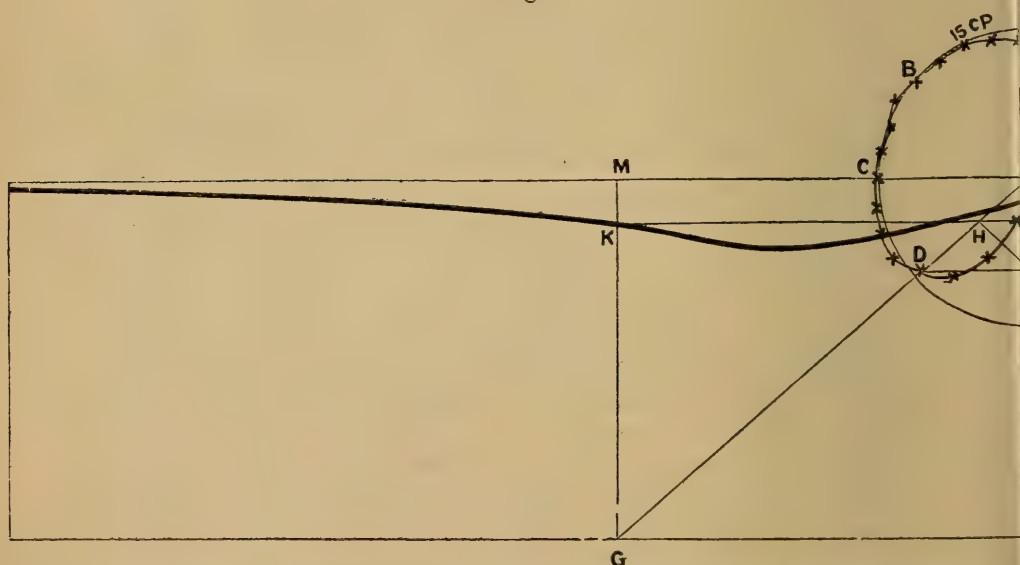
Let the illumination of the horizontal plane G E through E, produced by the source L, be required.

Draw a line M L through the source L parallel to the plane G E.

Through any point D, say, of the photometer-curve, draw D F parallel to the horizontal plane G E.

Join D L and produce to meet the horizontal plane in G.

Through F draw F H perpendicular to D L, and through H draw H K parallel to G E, meeting the vertical line G M in K.

The illumination at G is then equal to $MK/(MG)^2$, MK being measured on the same scale as the radii of the photometer-curve.

For the illumination at G $= \dfrac{\text{DL} \cdot \cos \widehat{\text{MGL}}}{\text{GL}^2}$. Multiply both sides by $(\text{LE})^2$,

$$\therefore \quad (\text{LE})^2 \ (\text{illumination at G}) = \text{DL} \cdot \left(\frac{\text{LE}}{\text{GL}}\right)^2 \cos \widehat{\text{MGL}}$$

$$= \text{DL} \cos^3 \widehat{\text{MGL}}$$

$$= \text{MK by the construction.}$$

Fig. 2.
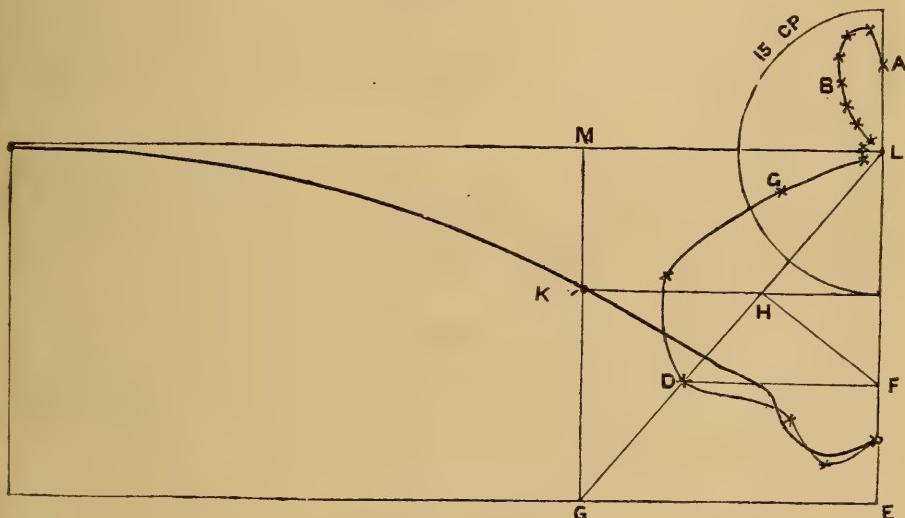
Fig. 3.
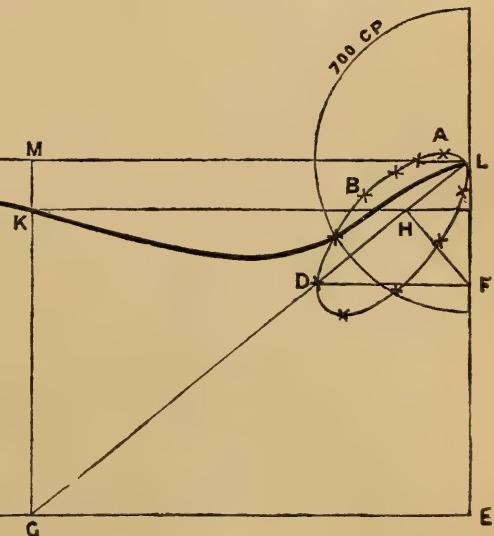
Hence the illumination at G due to the source L is proportional to the length intercepted between the horizontal line ML, and the curve passing through the points obtained at K is obtained.

The absolute value of the illumination at the point G due to the source L is equal to the illumination which would be produced if L were removed and a source of candle-power represented by MK on the same scale as LD were placed at M.

In order to show the applicability of the method, three photometer-curves are shown in figures 1, 2, and 3 ; the first being due to an Argand burner without shade, the second the same burner with a conical paper shade (from Dibdin's ' Photometry '), the third to an arc lamp (from Trotter's paper in the Journal Inst. Elect. vol. xxi. p. 365, 1892), and the illumination produced by each source on a horizontal plane is found*.

It is interesting to notice the great increase of illumination in the case of the Argand burner when the shade is introduced. In the case of the arc, the point on the horizontal when the illumination is a maximum is evidently at about 60° below the horizontal plane through the lamp.

XLI. *On Helium and its place in the Natural Classification of Elementary Substances.* By HENRY WILDE, *F.R.S.*†

[Plate VIII.]

THE announcement made by Professor Ramsay that a gas from the mineral *Cleveite* showed the yellow spectral line of solar helium λ 5876, and was therefore identical with that hypothetical element ‡, was received by physicists with some amount of incredulity, as it was illogical to predicate the identity of any element from the near coincidence of a single line among the numerous lines which belong to other elementary substances in the gaseous condition. Nevertheless, the conspicuous brightness and comparative isolation of the chromospheric line D_3, together with the statement by Crookes, that the yellow line of the cleveite gas was single §, in agreement with the reputed singleness of D_3, gave some force to the idea that the solar and terrestrial gases were identical. Lockyer ‖ and Runge¶, however, subsequently discovered that the yellow line of the new gas was double, and the latter observer justly remarked " that the unknown element helium, causing the line D_3 to appear in the solar spectrum, is not identical with the gas in cleveite unless D_3 is also shown to be double."

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* These curves have been kindly drawn for me by Mr. Julius Frith, Exhibition (1851) Scholar of the Owens College.
† A paper read before the Manchester Literary and Philosophical Society, October 1, 1895. Communicated by the Author.
‡ Chemical News, March 29, 1895.　　　　§ Ibid. p. 151.
‖ Proc. Roy. Soc. April 25, p. 69.
¶ Nature, June 6, p. 128.

Runge further observed that the less refrangible of the two lines was much weaker than the other, and he found the difference in the wave-lengths of the lines to be 0·323 tenth metres.

The doubleness of the yellow line of the cleveite gas led directly to a closer observation of the chromospheric line by Huggins[*], Lockyer, and Professor Hale of Chicago[†]. Each of these observers has found that the solar helium line is also double. Mr. T. Thorp of Whitefield, the inventor of several valuable spectroscopic appliances to the telescope, has also, by means of a Rowland grating of 14,438 lines to the inch, and a fourth-order spectrum, divided D_3. Through the kindness of Mr. Thorp, I have been able to confirm the observations which have, up to the present time, been made on the doubleness of the yellow line of solar helium.

Not only is the doubleness of the chromospheric line established, but its components are of unequal width, and the weaker line is on the least refrangible side of the spectrum as in the gas from cleveite. Prof. Hale has determined the difference in the wave-lengths of the components of D_3 to be 0·357. Moreover, Lockyer has observed that five other prominent lines of the new gas coincide with the chromospheric lines 7066, 6678, 5016, 4922, and 4472[‡]. The only question now open for discussion as to the identity of solar and terrestrial helium is the difference in the wave-lengths of the double line as determined by the several observers. Crookes, as we have seen, pronounced the yellow line of terrestrial helium to be single. Ramsay subsequently observed the line double, and estimated the distance between them to be $\frac{1}{50}$ part of that between the sodium lines[§] = 0·120 tenth metres. Runge and Paschen observed a difference of 0·323 between the components of the yellow line, while Prof. Hale, as I have said, makes the difference between the same components of solar helium 0·357.

In none of these observations of the characteristic yellow line of terrestrial and solar helium would any account appear to have been taken of the influence of pressure and diffusion with other gases, in varying the width of spectral lines, especially on the more refrangible side of the spectrum. I have already shown in my paper on the spectrum of thallium (Proc. Roy. Soc. 1893) that the expansiveness and brightness of the C line of hydrogen, at atmospheric pressure, masked completely one of the two principal lines in the

[*] Chemical News, July 19, p. 27.
[†] Nature, August 1, p. 327.
[‡] Proc. Roy. Soc. June 13, 1895.
[§] Paper read before the Chemical Society, June 20, 1895.

visible spectrum of thallium for more than thirty years, so that the sharp red line in the arc- and spark-spectrum of this element is not mapped in the recent tables of Thalén, and Kayser and Runge [*].

I have recently repeated some of the experiments of Ramsay and Lockyer on helium obtained by the distillation method from Norwegian cleveite, pitchblende, and other minerals containing uranium. The result of these experiments confirms the conclusion that the differences in the determination of the wave-lengths of the components of the characteristic yellow line are due to the same cause which masked the red line of thallium.

The apparatus with which the experiments were made is shown in Plate VIII. one-fourth the actual size. It consists of a small steel cylinder heated from below by a Bunsen burner, or the oxyhydrogen-flame. A bent iron tube, of small bore, connects the cylinder with an air-pump and a glass sparking-receiver in which the spectra of the gases are produced. The mouth of the receiver is plugged with a stopper of caoutchouc, through which a pair of iron wires are thrust terminating with platinum electrodes. Vacuum-gauges are mounted on the pump for measuring the amount of rarefaction in the cylinder and sparking-receiver to a small fraction of an inch of mercury.

An induction-coil giving a 10-inch spark in air was used in the experiments, and the density of the spark was increased by means of a Leyden jar. The observations were made with the same direct-vision spectroscope of five prisms as was used in my research on the spectrum of thallium.

The minerals, in coarse powder, from which the gases are to be distilled are fed into the cylinder through the end into which the tube is screwed, and the joint is afterwards made good by means of a washer of asbestos.

Dr. Burghardt, Lecturer on Mineralogy at the Owens College, kindly placed at my disposal some heavy zirconiferous sand, containing uranium, which is found in large deposits on the coast of Brazil. This sand is an abundant source of helium, and, judging from the brightness of the spectroscopic reaction, is not much inferior to that of cleveite.

14 grammes of the sand were fed into the cylinder, which, after being exhausted of air, was heated up by the Bunsen flame. As the heat of the cylinder approaches visible redness, the double sodium line and the C hydrogen line make their appearance, and when the pressure in the receiver increases to six inches of mercury the yellow line and the violet line

4472 of helium become visible. As the heat and pressure increase, the lines of hydrogen and helium widen out, till at a pressure of 15 to 26 inches the helium and sodium lines are nearly of equal width and appear as single lines in the spectrum.

This experiment shows that, within certain limits, the *distance* between the components of D_3 is not to be taken as the criterion of the identity of chromospheric and terrestrial helium.

As solar temperatures are much too high for the formation of chemical compounds, the coincidence of the characteristic lines of chromospheric and terrestrial helium clearly establishes the elementary nature of the gas or gases producing these lines. Lockyer has indicated in several papers [*] that the new gas obtained from *uraninite* by his distillation method is a mixture, and that some of the spectral lines common to the chromospheric and terrestrial gas may belong to two or more elementary substances. Profs. Runge and Paschen have made further progress in this direction by showing that the gas from cleveite, after being diffused through asbestos, gives two different spectra and is, consequently, a mixture [†]. One of these gases, from its more rapid diffusion, is considered to be less dense than the other. From a comparison of these spectra, the German physicists further conclude that the denser of the two gases, producing D_3, is helium proper, but the lighter constituent has not yet received a new name.

It may be of interest for me to note here that, when a strong induction-current is transmitted for a few minutes through a newly filled vacuum-tube of reputed helium, the red line 7066 disappears entirely from the spectrum, and all subsequent differences in the intensity of the discharge fail to reproduce it.

In my classification of elementary substances in multiple proportions of their atomic weights, each series or family is considered to be condensations of the typical elements H, H2, H3, H4, H5, H6, H7[‡]. That some, if not all, of these elements exist in a gaseous condition, and are of small specific gravity, appears to me to be highly probable. M. Langlet, of the University of Upsala, has found the density of the cleveite gas to be 2·02 ($H=1$)[§]; while the more recent determination of Ramsay has raised the density of reputed helium to 2·13. Should, however, the conclusions of Lockyer

[*] Proc. Roy. Soc., April 25, May 9, June 13, 1895.

[†] Paper read before the British Association at Ipswich; 'Nature,' September 26, 1895.

[‡] Memoirs Manchr. Lit. and Phil. Soc. 1878, 1887, 1895; Chem. News, vol. xxxviii. pp. 66, 96, 107.

[§] *Comptes Rendus,* June 4, 1895; Chem. Soc. Journal, June 20, 1895.

and Runge and Paschen be accepted, *i. e.* that the new gas is a mixture, the density of helium proper will be further increased.

The low specific gravity of the cleveite gas, and its occlusive affinity for the platinum electrodes of the vacuum-tubes during the transmission of the electric discharge, as first noticed by Lockyer[*], indicate that helium proper is the typical element H3 at the head of the uneven series H3n, homologous in position and analogous in properties with hydrogen, and that the lighter constituent of reputed helium is the typical element H2 at the head of the positive even series H2n. Further research, however, is necessary before the characteristic lines belonging to each of the constituents of reputed helium can be determined with certainty, and the complete separation of the other new gases obtained from minerals, by the distillation method, is the problem which awaits solution.

[†] I have shown in former papers that the characteristic spectral lines of the alkaline metals in the series Hn, and their homologues of position in the series H3n containing thallium and its analogues, indium and gallium, advance towards the more refrangible end of the spectrum in the inverse order of their atomic weights[‡]. The same relation is also observable in the spectra of the alkaline-earth metals, and in other well-defined series of elements. M. Lecoq de Boisbaudran had previously formulated the same relation towards the least refrangible end of the spectrum, in the direct order of the atomic weights[§].

Profs. Runge and Paschen, in their recent communication to the Berlin Academy[||], have pointed out that, while the spectra of each vertical series of chemically related elements like Li, Na, K, Rb, Cs, shift towards the least refrangible side of the spectrum with increasing atomic weight, the spectra of elements in homologous positions in each horizontal series like Na, Mg ; K, Ca; Cu, Zn ; Rb, Sr ; Ag, Cd, shift the opposite way, so that the spectrum of the element of greater atomic weight is, as a whole, situated on the more refrangible side. An examination of the spectra of the different elements will show that this generalization holds fairly good for the first and second series, and is also observable, but in a much less degree, in members of the third series. So great, however, is the difference of displacement

[*] Proc. Roy. Soc., June 13, 1895, p. 195.
[†] Note read before the Society, October 15, 1895.
[‡] Manchester Memoirs, 1878, 1887, 1895 ; Proc. Roy. Soc. 1893.
[§] *Comptes Rendus*, vol. lxix. 1869.
[||] Proceedings of the Berlin Academy, July 11, 1895, p. 757 ; Phil. Mag. September 1895 ; 'Nature,' Sept. 26.

between the spectra of the odd and even series, taken horizontally, that the spectra of members of the third series shift in the same relation to the second as the spectra of Li, Na, K, Rb, Cs, *i. e.* to the less refrangible side of the spectrum with increasing atomic weights. The same inversions of displacement are also observable in the spectra of the odd and even members of the vertical series Hn, $H2n$, $H3n$ as are found in the horizontal series; the spectra of the heavy elements, like Cu, Ag; Zn, Cd, shifting to the more refrangible side of the spectrum in relation to the alkaline and alkaline-earth metals on each side of them.

The spectra of members of the highest series of elements, both vertically and horizontally, shift, on the whole, towards the less refrangible side of the spectrum with increase of atomic weights, like the spectra of the alkaline metals.

Mendeléeff and others have pointed out the greater resemblance of chemical and other properties which odd or even series of elements have to each other than to the immediately adjoining series. Hence the spectra of Ga, In, Tl, in the third series, have a greater resemblance to the spectra of their homologues of position, K, Rb, Cs, in the first series, than they have to their homologues Ca, Sr, Ba, in the second (even) series. The chemical and other properties of hydrogen and the two constituents of reputed helium (H, H2, H3) may therefore be expected to stand in the same order to each other as their homologues of position in the first, second, and third vertical series of elements, Hn, $H2n$, $H3n$.

Profs. Runge and Paschen, in their endeavour to bring the two new gases into a classification in accordance with the requirements of Mendeléeff's so-called periodic law, have placed them in the first series between hydrogen and lithium, notwithstanding that they, at the same time, show that the spectra of these gases shift in the opposite direction to the spectra of the alkalies Li, Na, K, Rb, Cs.

The German physicists can hardly have realized the consequences to Mendeléeff's system by placing the two gases between hydrogen and lithium. In the paper which I read before the Society in December last I gave a demonstration of the confusion that would be brought into the so-called periodic system by the discovery of a new element x in the particular series where these physicists propose to place the new gases*. There is absolutely no place in Mendeléeff's system for elements with atomic weights between lithium and hydrogen, as the Russian chemist never contemplated the existence of elements with properties and cosmical relations such as the new gases have been found to possess.

* Memoirs Manchester Lit. and Phil. Society, vol. ix. p. 77.

XLII. *Self-recorded Breaks in the Properties of Solutions.*
By Spencer Umfreville Pickering, *F.R.S.*[*]

WHEN investigating the properties of solutions I was desirous of obtaining some method by which the more or less sudden changes of curvature noticed when these properties are plotted against strength might be made to register themselves automatically. Other work has prevented me from following up this subject ; but the method which was obtained seemed to be so satisfactory, that, although it may not be applicable in all cases, a brief note of some preliminary results may be of some interest : moreover it is so simple that anyone possessed of a delicate thermometer and efficient calorimeter can verify the existence of these changes of curvature at the expense of a day's work. The method consisted in running a solution into a calorimeter of water with a thermometer in it, and photographing the height of the mercury column on a revolving cylinder. The means for this photographing were not at hand at the time, and therefore the thermometer was read through a telescope every half minute instead. The solution was run in from a graduated bottle through a siphon ending in a very fine point and dipping under the surface of the water in the calorimeter. The amount of solution which had been run in was read off at intervals, and thus the composition of the liquid in the calorimeter at any moment could be deduced. The calorimetric liquid was stirred continuously by a stirrer worked by a water motor. The substance investigated was sulphuric acid.

If the heat of dissolution of different strengths of acid shows changes of curvature at certain points, as it does according to my previous work (Chem. Soc. Trans. 1890, p. 101), then the rate at which heat is evolved when the acid is run continuously into water must show changes of curvature also. Whether the latter will be recognizable or not will depend on the magnitude of the former changes, and also on their magnitude as compared with the total heat evolved.

As instances favourable for recognition, the well-marked breaks with very weak solutions of the acid were taken; a 5 or 10 per cent. solution being run into 550 cubic centim. of water.

I need only give two experiments as examples illustrating the existence of the two extreme breaks indicated by my former work.

Fig. 1 shows the results of one series. In the upper drawing the thermometer-readings are plotted against time, and in the lower the strength of the calorimetric liquid is

plotted against time. The dotted lines formed by the nume-
rous experimental points in the upper drawing have been
extended a little by continuous lines in order to make the

Fig. 1.
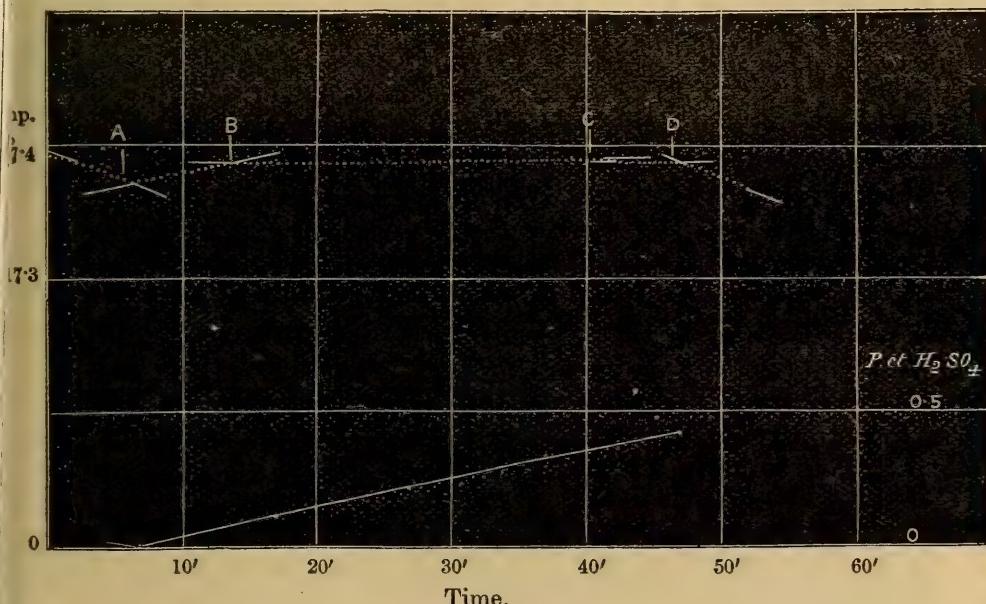
changes more easily discernible. To ascertain the strength
at which any change in the upper drawing has occurred, it
is only necessary to take the reading of the lower curve for
the same time. The temperature-readings form five lines
which within experimental error are absolutely straight, and
owing to the well-marked angles at which these lines meet,
and to the large number of experimental points on them (as
many as 55 in one case), there can be no doubt as to their
real nature. Of the four changes which this figure exhibits
two are incontestably breaks : A is the point at which the
stream of acid was started, and D that at which it was
stopped ; yet these are no better marked than those at B
and C, which, therefore, must equally be admitted to be
breaks.

Looking at the changes near A and D it will be seen that
these occur about one minute after the stream of acid was
started and stopped respectively ; this represents the time
taken by the acid to get mixed with the water, and the lag of
the thermometer behind the temperature of the liquid.

The break at C was not so well marked as it might have
been had the experiment been continued for a longer time.
Another experiment illustrated in fig. 2 shows it better.
Here, however, the stream of acid being faster, there were
not sufficient observations with the weakest liquid to show

satisfactorily the first break, B, although the existence of some irregularity in this region is perfectly evident. The lines in this figure are straight lines also, except the portion

Fig. 2.
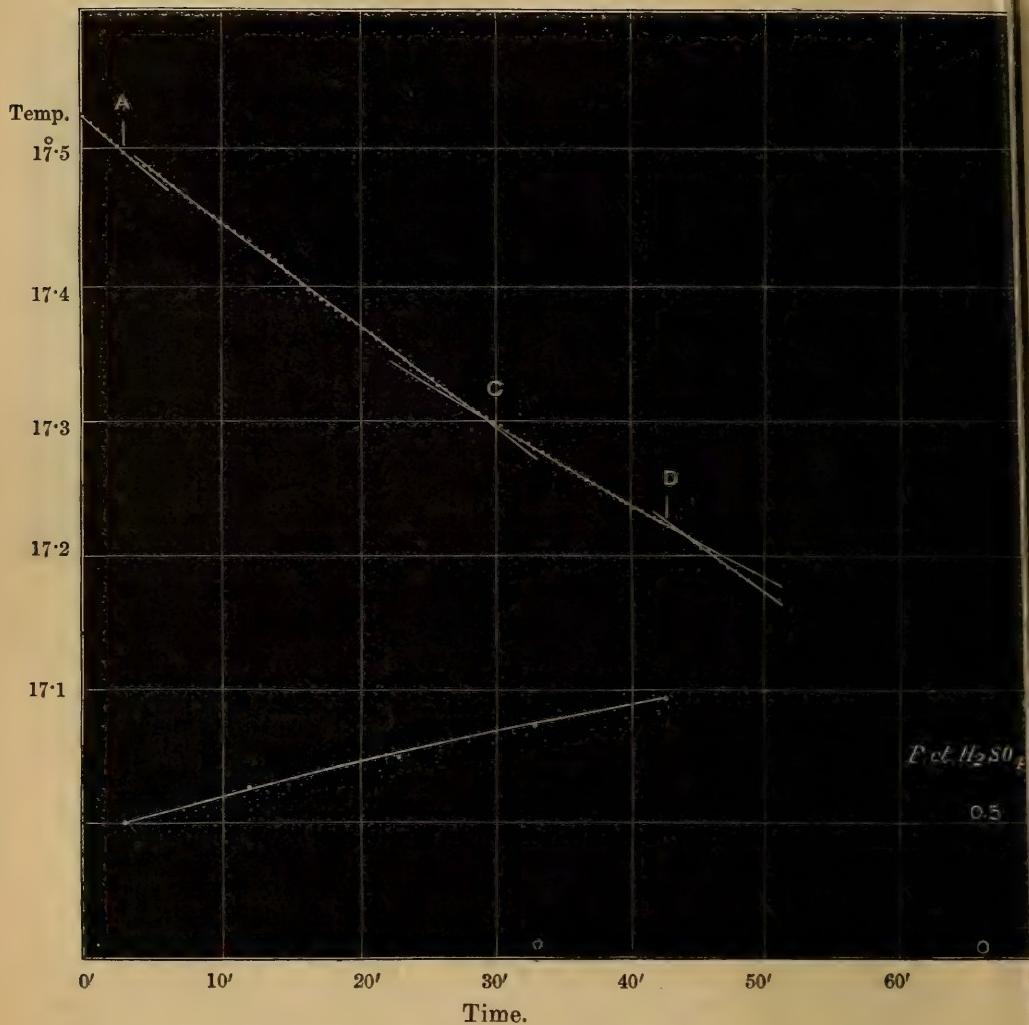
C D, where a very slight curvature is noticeable. The break accompanying the change in strength of the solution, C, is just as well marked as the undoubted breaks due to the starting and stopping of the stream of acid, A and D.

The determinations may be modified in many ways. The strength of the acid may be varied, or the liquid taken in the calorimeter may be acid of various strengths, instead of water : the rate at which the acid is added may be altered considerably, and, instead of being uniform, it may be accelerated or retarded during the addition, by connecting the bottle with another one, into which, or out of which, water is run at a rate greater than in the case of the acid. The form of the figure obtained in any particular determination admits also of exten-

sive modifications by altering the initial temperature, and, therefore, rate of cooling of the calorimeter ; but, obviously, the most satisfactory results will be obtained if matters are so adjusted that the figure is chiefly rectilineal, as in the cases here cited. Where, however, the total heat evolved is considerable, as it often is, with strong solutions, it is impossible to apply the method with sufficient accuracy to render it of any service.

The readings in the experiments quoted are given in the following table.

Readings of the Thermometer taken every half minute during the addition of a 5·5 per-cent. solution of sulphuric acid to water.

First Experiment.			Second Experiment.		
17°·3915	17°·3860	17°·3895	17°·5230	17°·3970	17°·2785 d
17·3910	17·3860	17·3900 d	17·5180	17·3940	17·2755
17·3890	17·3865	17·3900	17·5130	17·3905	17·2720
17·3875	17·3865	17·3900	17·5090	17·3865	17·2690
17·3865	17·3870	17·3905	17·5050	17·3830	17·2660
17·3855	17·3875	17·3905	17·5010	17·3790	17·2625
17·3840	17·3875	17·3905	17·4965 a	17·3760	17·2600
17·3820	17·3880	17·3905	17·4925	17·3725	17·2565
17·3805	17·3880	17·3905	17·4900	17·3680	17·2550
17·3785	17·3885	17·3910	17·4870	17·3650	17·2510
17·3770	17·3885	17·3910	17·4840	17·3610	17·2485
17·3755	17·3885	17·3910	17·4810	17·3570	17·2455
17·3740 a	17·3885	17·3900	17·4765	17·3535	17·2425
17·3723	17·3885	17·3900	17·4735	17·3500 c	17·2400
17·3720	17·3890	17·3890	17·4700	17·3460	17·2360
17·3735	17·3890	17·3890	17·4660	17·3415	17·2330
17·3745	17·3890 c	17·3885	17·4620	17·3380	17·2315
17·3755	17·3890	17·3885	17·4580	17·3345	17·2285
17·3765	17·3890	17·3885	17·4545	17·3310	17·2260
17·3775	17·3890	17·3885	17·4505	17·3255	17·2225
17·3785	17·3890	17·3885	17·4465	17·3220	17·2205 e
17·3800	17·3890	17·3885 e	17·4425	17·3185	17·2170
17·3810	17·3890	17·3880	17·4390	17·3155	17·2140
17·3815	17·3890	17·3875	17·4360	17·3115	17·2115
17·3825	17·3890	17·3865	17·4320	17·3075	17·2070
17·3835	17·3890	17·3850	17·4285	17·3040	17·2035
17·3840	17·3890	17·383)	17·4255 b	17·3010	17·2010
17·3845	17·3890	17·3810	17·4215	17·2980	17·2965
17·3850	17·3890	17·3790	17·4175	17·2950	17·2930
17·3850	17·3890	17·3770	17·4130	17·2910	17·2890
17·3855	17·3890	17·3755	17·4085	17·2870	17·2855
17·3855	17·3895	17·3730	17·4050	17·850	17·2925
17·3860 b	17·3895	17·3715	17·4005	17·820	17·2895
17·3860	17·3895	17·3700			
17·3860	17·3895				

a. Stream of acid started.

b, c, d, e. Composition of the liquid after these readings, 0·112, 0·215, 0·327, and 0·418 *per cent.* H_2SO_4 respectively.

e. Stream of acid stopped.

a. Stream of acid started.

b, c, d, e. Composition of the liquid after these readings, 0·132, 0·248, 0·359, and 0·457 *per cent.* H_2SO_4 respectively.

e. Stream of acid stopped.

Although these determinations were only of a preliminary character, and the bottle from which the acid was supplied was graduated but roughly, yet the breaks shown by the results are in perfect agreement with those indicated by my former work. Fig. 1 shows breaks at 0·08 and 0·38 *per cent.* of acid (allowing for the one-minute lag of the thermometer), and fig. 2 places the latter at 0·33 per cent., mean 0·355 : whereas my heat of dissolution determinations gave breaks at 0·1 and 0·4 *per cent.* (*loc. cit.* p. 127), and the most probable positions of these, as deduced from the freezing-points and all the other properties examined together (*loc. cit.* p. 352), were 0·087 and 0·345 per cent. respectively.

XLIII. *Intelligence and Miscellaneous Articles.*

MEASUREMENTS WITH ALTERNATING CURRENTS OF HIGH FREQUENCY. BY DR. JOSEF TUMA.

THE author determines the resistance of copper, german silver, nickel, and iron wires for oscillating currents. He uses two Bunsen ice-calorimeters with thin glass tubes passing completely through them instead of test-tubes. In the tube of one calorimeter is introduced the piece of wire to be investigated, and in the other a resistance constructed of a thin (0·001—0·010 millim.) tubular layer of silver or copper deposited on glass.

By preliminary experiments it is ascertained that the alternating currents used (84,400—232,900 oscillations in a second) have the same density of current throughout the whole section. Alternating currents are sent through the two calorimeters arranged in series, or steady currents for the purpose of graduation, and from every two pairs of such readings the strength of the alternating current and the ratio w'/w of the resistances of wires for alternating and steady currents were measured.

Values were obtained which only approximately agree with the formulas developed by Stefan, for they presuppose far higher numbers of vibrations than those used here. The author could not produce such rapid vibrations, for it was necessary to add to the short wires to be measured a high calculable self-induction ; otherwise the number of vibrations would vary according to the resistances to be determined, and they would moreover be very difficult to calculate. It could always be seen that, for alternating currents of high frequency, the agreement was more complete for non-magnetizable conductors. For magnetic substances calculations are illusory, owing to the variability of the permeability. The author observed in the case of iron wires that the resistance varied with the strength of the alternating current, decreasing as the current increased.— *Wiener Berichte,* June 14, 1895.

XLIV. *Molecular Force and the Surface-Tension of Solutions.*
By William Sutherland[*].

IN "The Surface-Tension of Mixed Liquids" (Phil. Mag. Aug. 1894) it was shown that for a mixture of liquids 1 and 2 containing in one gramme p_1 gramme of 1 and p_2 of 2, the surface-tension α and the density ρ are connected with the corresponding quantities for the two liquids by the relation

$$\alpha/\rho^2 = p_1^2\alpha_1/\rho_1^2 + p_2^2\alpha_2/\rho_2^2 + \frac{2\,_1A_2}{(_1A_{12}A_2)^{\frac{1}{2}}} p_1 p_2 \left(\frac{\alpha_1\alpha_2}{\rho_1^2\rho_2^2}\right)^{\frac{1}{2}} \frac{(m_1/\rho_1)^{\frac{1}{3}} + (m_2/\rho_2)^{\frac{1}{3}}}{2(m_1/\rho_1)^{\frac{1}{3}}(m_2/\rho_2)^{\frac{1}{3}}}, \quad (6)$$

where $3\,_1A_1 m_1^2/r^4$, $3\,_2A_2 m_2^2/r^4$, and $3\,_1A_2 m_1 m_2/r^4$ express the molecular force between molecules of 1 and 1, 2 and 2, and 1 and 2 at distance r apart. It was also shown by experiment that for most pairs of normal liquids $_1A_2^2 = {_1A_{12}}A_2$, and as we have approximately $(m_1/\rho_1)^{\frac{1}{3}} + (m_2/\rho_2)^{\frac{1}{3}} = 2(m_1/\rho_1)^{\frac{1}{3}}(m_2/\rho_2)^{\frac{1}{3}}$, we get

$$\alpha/\rho^2 = (p_1\alpha_1^{\frac{1}{2}}/\rho_1 + p_2\alpha_2^{\frac{1}{2}}/\rho_2)^2. \quad \cdots \quad (7)$$

The experimental proof of the relation $_1A_2^2 = {_1A_{12}}A_2$ consisted in showing that for mixtures of 24 out of 28 pairs of liquids the ratio $_1A_2/(_1A_{12}A_2)^{\frac{1}{2}}$ had a value between ·9 and 1·1. We can make the proof more complete by means of some data determined by Prof. Ramsay and Miss Aston (Proc. Roy. Soc. lvi.). In the following table the first liquid of each pair is 1,

[*] Communicated by the Author.

and the second is 2, and as $p_1 = 1 - p_2$, only p_2 is given. The surface-tensions are expressed in dynes per centim. :—

TABLE I.

Toluene and Piperidine at 15°·2 C.

ρ_1.	α_1.	ρ_2.	α_2.	p_2.	ρ.	α.	$_1A_2/(_1A_1\,_2A_2)^{\frac{1}{2}}$.
·8682	28·18	·8670	29·67	·156	·8677	28·55	1·02
				·822	·8674	29·43	1·00

Benzene and Carbon Tetrachloride at 11°·8 C.

·8865	29·13	1·6063	27·03	·6633	1·267	28·29	1·00
				·77	1·3533	27·83	1·01

Chlorobenzene and Ethylene Dibromide at 10°.

1·1176	33·65	2·192	39·22	·6253	1·6064	35·38	·97

Chloroform and Carbon Disulphide at 10°.

1·5077	27·62	1·277	32·73	·3892	1·4009	29·09	·98

It may be taken as proved that in the normal case

$$_1A_2 = (_1A_1\,_2A_2)^{\frac{1}{2}}.$$

If we apply the formula (6) just as it stands to aqueous solutions of substances which are solid at 15° C., the usual temperature of experiment; on solutions, we have to deal with the surface-tension α_2 of solids, which up to the present has not been measured; but we need not concern ourselves with this fact for α_2 stands for $k\,_2A_2\rho_2^2(m_2/\rho_2)^{\frac{1}{3}}$, where k is the same for all bodies at all temperatures if ρ_2 is the density in the surface-layer whose tension is measured, but if ρ_2 is the density in the body of the substance, then k becomes a function of temperature.

As water has many peculiarities we cannot assume that for water and any substance dissolved in it, $_1A_2 = (_1A_1\,_2A_2)^{\frac{1}{2}}$, but if water is 1 and the dissolved substance 2, then in (6) α_1/ρ_1^2 is a constant, a say, and for different solutions of the same substance α_1/ρ_2^2 is also a constant, say b, and in the last term the coefficient of p_1p_2 is a constant $2c$ say, then

$$\alpha/\rho^2 = ap_1^2 + bp_2^2 + 2cp_1p_2,$$
$$\alpha/\rho^2 - \alpha_1/\rho_1^2 = 2(c-a)p_2 + (a+b-2c)p_2^2. \quad . \quad . \quad (8)$$

We can show by Volkmann's data (Wied. *Ann.* xvii.) that this is a suitable form to express the relation between the surface-tension of a solution and its concentration : thus in the case of NaCl we get the values $a + b - 2c = 6·7$, $2(a-c) = 7·67$, and as $a = 7·44$, b and c are determined. The values of the surface-tension given by these constants in (8) are compared with the experimental in the following. In

the rest of this paper surface-tensions are given in mgrms. weight per millim.

TABLE II.

NaCl solutions at 20° C.

p_2	·255	·214	·144	·101	·052	0·0
ρ	1·1932	1·1596	1·1074	1·0720	1 0360	1·000
a exper.	8·41	8·20	7·89	7·74	7·61	7·44
a calcul.	8·42	8·22	7·93	7·73	7·57	

For $CaCl_2$ the values are $a+b-2c=8\cdot7$, and $2(a-c)=9\cdot48$, whence the comparison :—

CaCl₂ solutions at 19° C.

p_2	·360	·294	·200	·1135	·065	·024	0·0
ρ	1·3511	1·2773	1·1789	1·0971	1·0540	1·0179	1·00
a exper.	9·31	8·84	8·22	7·81	7·61	7·51	7·45
a calcul.	9·41	8·83	8·21	7·81	7·63	7·48	

These comparisons show that the form (8) is competent to represent the experimental facts, for the differences between the two sets of values of α lie within the limits of experimental error ; the difference between 9·31 and 9·41 for the most concentrated of the $CaCl_2$ solutions seems large, but the experimental difficulties of measurement increase as the saturation point is approached.

With the values just given for the coefficients in (8) we get for NaCl :—

$$a=\alpha_1/\rho_1^2=7\cdot44, \quad b=\alpha_2/\rho_2^2=6\cdot47, \quad c=\frac{{}_1A_2}{({}_1A_{1\,2}A_2)^{\frac{1}{2}}}\left(\frac{\alpha_1\alpha_2}{\rho_1^2\rho_2^2}\right)^{\frac{1}{2}}=3\cdot61,$$

so that
$$ {}_1A_2/({}_1A_{1\,2}A_2)^{\frac{1}{2}}=\cdot52 ; $$

similarly for $CaCl_2$ it is   .   .   .   ·38.

Thus it appears that for water and such substances as NaCl and $CaCl_2$ the relation ${}_1A_2^2={}_1A_{1\,2}A_2$ does not hold good ; but we must remember that as the peculiarities of water are largely due to its molecules being paired, it is possible that the addition of a dissolved substance may cause the breaking up of some of the pairs and so cause the solution to be really a mixture of three substances, and yet the form of our equation (8) might meet the circumstances of such a case although the meaning of the coefficients might be altered ; thus we cannot at present be sure that b as derived from experiments is really

α_2/ρ_2^2, and c really $\frac{{}_1A_2}{({}_1A_{1\,2}A_2)^{\frac{1}{2}}}\left(\frac{\alpha_1\alpha_2}{\rho_1^2\rho_2^2}\right)^{\frac{1}{2}}$.   Under these circum-

stances it seems best to study first all the values of b and c obtainable from Volkmann's data.

TABLE III.

	NaCl.	KCl.	NaNO$_3$.	KNO$_3$.	MgCl$_2$.	CaCl$_2$.	SrCl$_2$.	BaCl$_2$.
b	6·47	3·8	4·6	3·13	6·5	6·67	4·6	1·2
c	3·61	3·8	2·7	3·33	2·9	2·71	1·7	1·8

	Na$_2$CO$_3$.	K$_2$CO$_3$.	Na$_2$SO$_4$.	K$_2$SO$_4$.	MgSO$_4$.	ZnSO$_4$.	CuSO$_4$.
b	9·1	6·68	5·5	18·2	7·9	5·2	7·3
c	·8	1·80	1·8	1·6	·8	·2	·2

Now $\alpha_2/\rho_2{}^2$ is proportional to $_2A_2(m_2/\rho_2)^{\frac{1}{3}}$, so that m being actual mass and M the mass when the atom of H is 1 $(\alpha_2^{\frac{1}{2}}/\rho_2)\,M_2(M_2/\rho_2)-\frac{1}{6}$ is proportional to $(M_2{}^2\,_2A_2)^{\frac{1}{2}}$, and therefore to $(M_2{}^2l_2)^{\frac{1}{3}}$, the form under which the parameters of molecular attraction have been studied in my previous papers ; therefore if b is really $\alpha_2/\rho_2{}^2$, then $b^{\frac{1}{2}}M_2(M_2/\rho_2)-\frac{1}{6}$ is proportional to $(M_2{}^2l_2)^{\frac{1}{2}}$. In " Further Studies on Molecular Force " (Phil. Mag. Jan. 1895) the values of $(M_2{}^2l_2)^{\frac{1}{2}}$ for most of the above substances are given, either as calculated from their surface-tensions at the melting-point, or according to the Kinetic Theory of Solids. In the next table are given the values by the latter method from tables xiii., xiv., xix., and xxi. of " Further Studies," as well as values of M_2/ρ_2 and the ratio $b^{\frac{1}{2}}M_2/(M_2/\rho_2)-\frac{1}{6}\div(M_2{}^2l_2)^{\frac{1}{2}}$ in the last row.

TABLE IV.

	NaCl.	KCl.	NaNO$_3$.	KNO$_3$.	MgCl$_2$.	CaCl$_2$.
M_2/ρ_2	27·3	38·3	39·0	48·8	43·6	50·0
$(M_2{}^2l_2)^{\frac{1}{2}}$ ...	5·7	6·8	7·1	8·3	7·3	7·9
	15·1	11·6	13·9	11·3	17·7	18·9

	SrCl$_2$.	BaCl$_2$.	Na$_2$CO$_3$	K$_2$CO$_3$.	Na$_2$SO$_4$.	K$_2$SO$_4$.
M_2/ρ_2	51·9	54·1	43·0	60·0	54·0	66·0
$(M_2{}^2l_2)^{\frac{1}{2}}$ ...	8·7	9·5	6·2	7·6	7·8	8·9
	20·2	12·3	19·5	16·8	15·5	29·4

The mean value of the ratio for the compounds of the monad metals with the monobasic acid radicals is 13, and for the others involving either dyad metal or dibasic acid radical the mean value is 19, which is half as large again as 13; but the departures from the mean such as 12·3 for BaCl$_2$, and 29·4 for K$_2$SO$_4$ are too large to allow us to determine whether $b^{\frac{1}{2}}M_2(M_2/\rho_2)-\frac{1}{6}$ as determined from solutions is proportional to $(M_2{}^2l_2)^{\frac{1}{2}}$ as determined from the solid, but they do not determine that the proportionality does not exist, because b being the coefficient of the smallest term in (8) is very seriously affected by experimental error or slight defect in the

theoretical equations. There is no theoretical reason why there should be the two values 13 and 19 for the ratio unless it be that b is not strictly $\alpha_2/\rho_2{}^2$. But in the next comparison to which we proceed we can see more light as to the meanings of b and c; for if c is really $_1A_2(\alpha_1\alpha_2)^{\frac{1}{2}}/\rho_1\rho_2(_1A_1{}_2A_2)^{\frac{1}{2}}$, then ($\alpha_1$ being 7·5 and ρ_1 being 1·0) $c(\rho_1/\alpha_1{}^{\frac{1}{2}})M_2(M_2/\rho_2)-\frac{1}{6} \div (M_2{}^2l_2)^{\frac{1}{2}}$ should be proportional to $_1A_2/(_1A_1{}_2A_2)^{\frac{1}{2}}$; the values of this ratio are :—

<p style="text-align:center">Table V.</p>

NaCl.	KCl.	NaNO₃.	KNO₃.	MgCl₂.	CaCl₂.
7·8	8·3	6·4	7·7	7·4	7·2

SrCl₂.	BaCl₂.	Na₂CO₃.	K₂CO₃.	Na₂SO₄	K₂SO₄.
5·8	7·4	1·9	4·3	4·35	4·0

The ratio for all the compounds of the monobasic acid radicals is approximately constant with a mean value 7·25, while for the compounds of the dibasic acid radicals excepting Na_2CO_3 the ratio is near the mean 4·2 (Volkmann draws attention to the difficulty of getting reliable measurements of the surface-tension of solutions of Na_2CO_3). There is enough regularity in these results to show that the values of c are probably $_1A_2(\alpha_1\alpha_2)^{\frac{1}{2}}/\rho_1\rho_2(_1A_1{}_2A_2)^{\frac{1}{2}}$, and that therefore the irregularities in Table IV. are probably due to experimental error or to some minor theoretical imperfection in (8) which would have a large disturbing effect on the sensitive b. There is no *a priori* reason why $_1A_2/(_1A_1{}_2A_2)^{\frac{1}{2}}$ (and therefore the last ratio) should have the same value for different types of compound, so that there is nothing inconsistent with theory in the occurrence of the two values 7·25 and 4·2, whereas the two values 13 and 19 in Table IV. are inconsistent unless the difference between them is due to causes not taken account of in (8). It is a curious fact that the ratio

$$c(\rho_1/\alpha_1{}^{\frac{1}{2}})M_2(M_2/\rho_2)-\tfrac{1}{6} \div (M_2{}^2l_2)^{\frac{1}{2}}$$

for compounds such as $MgCl_2$ should range itself with that for Na_2SO_4, while the ratio $b^{\frac{1}{2}}M_2(M_2/\rho_2)-\frac{1}{6} \div (M_2{}^2l_2)^{\frac{1}{2}}$ for the type $MgCl_2$ detaches itself from that for the type Na_2SO_4. If b is really $\alpha_2/\rho_2{}^2$ and c is $_1A_2(\alpha_1\alpha_2)^{\frac{1}{2}}/\rho_1\rho_2(_1A_1{}_2A_2)^{\frac{1}{2}}$, then the ratio of the ratios gives the value of $_1A_2/(_1A_1{}_2A_2)^{\frac{1}{2}}$, which for the compounds of monad metal with monobasic acid radical is 7·25/13 or ·56, for compounds of dyad metal with dibasic acid 7·25/19 or ·38, and for compounds of monad metals with dibasic acids 4·2/19 or ·22. But we will return to these points later on.

If we desire to test our conclusions so far by applying them to other substances, we find ourselves somewhat restricted,

because most of the available experiments relate to comparatively dilute solutions, and to only one concentration, or to concentrations which vary but little. Under these circumstances the term in $p_2{}^2$ in (8) becomes small compared to that in $p_1 p_2$, but not so small that it can be actually neglected ; we can take account of it approximately by writing (8) in the form

$$\alpha/\rho^2 = p_1{}^2\alpha_1/\rho_1{}^2 + \frac{2_1A_2}{(_1A_{12}A_2)^{\frac{1}{2}}}p_1p_2\alpha_1^{\frac{1}{2}}\alpha_2^{\frac{1}{2}}/\rho_1\rho_2 + \frac{_1A_2{}^2}{_1A_{12}A_2}p_2{}^2/\rho_2{}^2\,(_1A_2{}^2/_1A_{12}A_2)$$

and then in the last part of the last term give $_1A_2{}^2/_1A_{12}A_2$ the values we have found, namely, $\cdot56^2$ for the type NaCl, $\cdot38^2$ for the type $MgCl_2$, and $\cdot22^2$ for the type Na_2SO_4 ; with these values the last equation becomes a quadratic for $_1A_2\alpha_2^{\frac{1}{2}}/\rho_2(_1A_{12}A_2)^{\frac{1}{2}}$ if the surface-tension α and the density ρ have been measured for a solution of strength p_2.

Thus for the haloid compounds of Li, Na, and K and their nitrates we have

$$\alpha/\rho^2 = p_1{}^2\alpha_1/\rho_1{}^2 + \frac{2_1A_2}{(_1A_{12}A_2)^{\frac{1}{2}}}p_1p_2\alpha_1^{\frac{1}{2}}\alpha_2^{\frac{1}{2}}/\rho_1\rho_2 + \frac{1}{\cdot56^2}\frac{_1A_2{}^2}{_1A_{12}A_2}p_2{}^2\alpha_2/\rho_2{}^2, \quad (1$$

which with Röntgen and Schneider's data (Wied. *Ann.* xxix.) gives the following values for $_1A_2\alpha_2^{\frac{1}{2}}/\rho_2(_1A_{12}A_2)^{\frac{1}{2}}$, and for the ratio of $M_2(M_2/\rho_2) - \frac{1}{2}{}_1A_2\alpha_2^{\frac{1}{2}}/\rho_2(_1A_{12}A_2)^{\frac{1}{2}}$ to $(M_2{}^2l_2)^{\frac{1}{2}}$ given in the last row.

Röntgen and Schneider's measurements were made at about 18° C., and their values of α are given in an arbitrary unit which makes that for water 111·45, but taking this in mgrm. per millim. as 7·464 according to Volkmann, all Röntgen and Schneider's values of α for solutions can be expressed in mgrm. per millim.

TABLE VI.

	LiCl.	LiBr.	LiI.	LiNO$_3$.	NaCl.	NaBr.
p_2	·060	·115	·167	·094	·080	·134
ρ	1·033	1·087	1·138	1·056	1·057	1·111
a	7·698	7·66	7·58	7·645	7·702	7·679
$_1A_2\alpha_2^{\frac{1}{2}}/\rho_2(_1A_{12}A_2)^{\frac{1}{2}}$	1·89	1·05	·80	1·43	1·33	·90
$(M_2{}^2l_2)^{\frac{1}{2}}$	4·5	5·1	6·0	6·0	5·6	6·2
	10·7	10·3	9·7	9·4	8·0	8·3

	NaI.	NaNO$_3$.	KCl.	KBr.	KI.	KNO$_3$.
p_2	·183	·113	·100	·151	·199	·131
ρ	1·161	1·078	1·064	1·118	1·166	1·085
a	7·621	7·647	7·685	7·661	7·605	7·625
$_1A_2\alpha_2^{\frac{1}{2}}/\rho_2(_1A_{12}A_2)^{\frac{1}{2}}$	·745	1·18	1·37	·966	·82	1·22
$(M_2{}^2l_2)^{\frac{1}{2}}$	7·1	7·1	6·7	7·3	8·2	8·2
	8·4	7·7	8·4	8·4	8·5	7·8

The values of $(M_2{}^2l_2)^{\frac{1}{2}}$ just given have not been taken directly from the tables of " Further Studies," but have been obtained on the principle there established that in $(M_2 l)^{\frac{1}{2}}$ the atoms have the values Li 2·4, Na 3·5, K 4·6, Cl 2·1, Br 2·7, I 3·6, and NO_3 3·6. The values of M_2/ρ_2 are given in " Further Studies." In the last table the values of the ratio in the last row are rather high for the Li compounds, but for the Na and K compounds they agree with those in Table V., though rather higher than the mean 7·25, which we shall see to have been rather too small.

The equation to apply to Röntgen and Schneider's data for the compounds of these metals with CO_3 and SO_4 is

$$\alpha/\rho^2 = p_1{}^2\alpha_1/\rho_1{}^2 + \frac{2_1A_2}{(_1A_{1\,2}A_2)^{\frac{1}{2}}}\, p_1 p_2 \alpha_1^{\frac{1}{2}}\alpha_2^{\frac{1}{2}}/\rho_1\rho_2 + \frac{1}{\cdot 22^{\frac{1}{2}}}\frac{_1A_2{}^2}{_1A_{1\,2}A_2}p_2{}^2\alpha_2/\rho_2{}^2, \quad (11)$$

and in the following table the values of $(M_2{}^2l_2)^{\frac{1}{2}}/2^{\frac{1}{2}}$ are taken from table xxi. of " Further Studies," where they are denoted by ΣF_e;—

Table VII.

	Li_2SO_4.	Na_2SO_4.	Na_2CO_3.	K_2SO_4.	K_2CO_3.
p_2	·076	·096	·074	·115	·094
ρ	1·064	1·088	1·075	1·097	1·085
a	7·658	7·651	7·752	7·651	7·750
$_1A_2a_2^{\frac{1}{2}}/\rho_2(_1A_{1\,2}A_2)^{\frac{1}{2}}$ ...	·80	·60	·66	·68	·75
$(M_2{}^2l_2)^{\frac{1}{2}}/2^{\frac{1}{2}}$	7·3	7·8	6·2	8·9	7·6
	4·4	4·0	4·3	4·7	4·8

The values of the ratio in the last row agree well with those we found in Table V., from Volkmann's data ; Na_2CO_3 does not appear as an exception as it did before.

For the haloid compounds of the dyad metals Valson's data are available (*Comp. Rend.* lxxiv.) for use in the equation

$$\alpha/\rho^2 = p_1{}^2\alpha_1/\rho_1{}^2 + \frac{2_1A_2}{(_1A_{1\,2}A_2)^{\frac{1}{2}}}p_1 p_2 \alpha_1^{\frac{1}{2}}\alpha_2^{\frac{1}{2}}/\rho_1\rho_2 + \frac{1}{\cdot 38^2}\frac{_1A_2{}^2}{_1A_{1\,2}A_2}p_2{}^2\alpha_2/\rho_2{}^2. \quad (12)$$

Valson's values of α are given in an arbitrary unit, according to which the value for water is 60·8, while in mgrm. per millim. it is 7·464, so that all Valson's values for solutions can be expressed in mgrm. per millim. The values of $(M_2{}^2l_2)^{\frac{1}{2}}$ are reckoned on the principle established in " Further Studies," that $(M^2l)^{\frac{1}{2}}/2^{\frac{1}{2}}$ for this type of compound is the sum of parts $F_r/2$ due to the metal R, and F_s due to the halogen S, $F_r/2$ having the following values (" Further Studies," table xvii.), Mg 2·7, Ca 3·2, Sr 3·7, and Ba 4·2, while as before F_s for Cl is 2·1, Br 2·7, and I 3·6. For the Zn and Cd compounds $(M_2{}^2l_2)^{\frac{1}{2}}$ is taken from table xiv. The values of (M_2/ρ_2) are also given in " Further Studies."

Table VIII.

	MgCl$_2$.	CaCl$_2$.	CaBr$_2$.	CaI$_2$.	SrCl$_2$.
p_2	·045	·053	·091	·128	·074
ρ	1·035	1·042	1·077	1·106	1·064
a	7·588	7·599	7·563	7·514	·7·599
$_1A_2a_2^{\frac{1}{2}}/\rho_2(_1A_{1\,2}A_2)^{\frac{1}{2}}$	1·09	1·04	·71	·67	·76
$(M_2^2l_2)^{\frac{1}{2}}$	6·8	7·5	8·3	9·6	8·2
	8·1	8·0	8·7	9·9	7·6

	BaCl$_2$.	ZnCl$_2$.	CdCl$_2$.	CdBr$_2$.	CdI$_2$.
p_2	·095	·064	·084	·120	·155
ρ	1·088	1·056	1·078	1·113	1·142
a	7·612	7·551	7·588	7·514	7·452
$_1A_2a_2^{\frac{1}{2}}/\rho_2(_1A_{1\,2}A_2)^{\frac{1}{2}}$	·62	·66	·58	·46	·48
$(M_2^2l_2)^{\frac{1}{2}}$	8·9	5·9	7·5	8·5	9·1
	7·5	8·0	7·4	7·5	9·3

Here the ratio in the last row agrees well with the values for the compounds of Na and K with monobasic acid radicals; the mean value of the ratio for all the metallic compounds having a value near 8 is 8·5, and for compounds of the monad metals with the dibasic acids CO_3 and SO_4 it is 4·4, which is nearly one-half of 8·5. The value 8·5 obtained from Röntgen and Schneider's and Valson's experiments being larger than 7·25, would, if used in place of the 7·25, increase our factors ·56 and ·38, but as in the equations (10) and (11) we have used them only in the small term, the difference caused by the alteration may be neglected for the present.

Special interest would attach to the case of compounds of the type $ZnSO_4$, where a dyad metal is combined with a dibasic acid, but a reference to Table III. will show that c is so small that no great reliance can be placed on its value unless derived from a specially accurate and carefully checked set of experiments made for the purpose. But if we take the values of b and c as they stand in Table III. for $MgSO_4$ and $ZnSO_4$, and make the same comparisons as for other compounds, we get:—

Table IX.

	MgSO$_4$.	ZnSO$_4$.
M_2/ρ_2.........	44	50
$(M_2^2l_2)^{\frac{1}{2}}/2^{\frac{1}{2}}$...	6 8	5·8
$b^{\frac{1}{2}}M_2(M_2/\rho_2)-\frac{1}{6}\div(M_2^2l_2)^{\frac{1}{3}}$	18·7	23·4
$c(\rho_1/a_1^{\frac{1}{2}})M_2(M_2/\rho_2)-\frac{1}{6}\div(M_2^2l_2)^{\frac{1}{3}}$	1·95	·75

The values of $(M_2^2l_2)^{\frac{1}{2}}/2^{\frac{1}{2}}$ are given on the assumption that for this type of compound they are the sums of parts $F_r/2$

and $F_s/2$ due to metal and acid respectively, with the values
2·7 for Mg, 1·7 for Zn, and 4·1 for SO_4. Whether this
assumption is true has still to be decided ; it is made here
only to see to what results it leads, and as it gives the ratios
$b^{\frac{1}{2}}M_2(M_2/\rho_2)^{-\frac{1}{6}} \div (M_2{}^2l_2)^{\frac{1}{2}}$ with values 18·7 and 23·4, not far
from the 19 characteristic of the types $MgCl_2$ and Na_2SO_4,
we have a certain amount of encouragement for believing our
assumption to be true, but our values of the ratio are not
reliable enough to make us sure. As regards

$$c(\rho_1/\alpha_1{}^{\frac{1}{2}})M_2(M_2/\rho_2)^{-\frac{1}{6}} \div (M_2{}^2l_2)^{\frac{1}{2}},$$

the smallness of c causes it to be unreliable. If we made
the guess that as for the types NaCl and $MgCl_2$ the ratio is
8·5, and for the type Na_2SO_4 it is 4·4, so for the type $MgSO_4$
it is 2·2, we should not involve ourselves in an error greater
than the experimental ones, but the final decision of the point
must rest with special experiments. It is obvious that we
can hardly draw any reliable inferences from experiments on
the surface-tension of dilute solutions of compounds of the
type $ZnSO_4$ unless they are of a very high degree of accuracy,
because c being small and $p_2{}^2$ small, the value of $\alpha/\rho^2 - \alpha_1/\rho_1{}^2$
is small.

When we come to treat of solutions of organic compounds
we have to separate them into two classes, the exceptional and
the normal. Traube's experiments (*Ber. d. deutsch. Chem.
Ges.* xvii.; *Ann. der Chem.* cclxv.) show that mixtures of water
with the alcohols and fatty acids are exceptional, the most
pronouncedly exceptional case being that of water and amyl
alcohol, for 2·5 per cent. of amyl alcohol in water reduces the
surface-tension to 2·8, that for the pure alcohol being 2·4 and
for water 7·3. The probable cause for the exceptional be-
haviour of these mixtures is a difference of composition in the
surface-layers from that in the body of the liquid. Certain
other solutions of organic compounds appear to behave nor-
mally as regards surface-tension, and for them Traube's data
(*Journ. f. prak. Chem.* cxxxix.) are given in the following
table. The values of $(M_2{}^2l_2)^{\frac{1}{2}}$ have not been directly deter-
mined for any of these substances, but they can be estimated
according to the values given for the different atoms and
radicals on pp. 4 and 7 of " Further Studies," although on
account of the exceptional nature of the alcohols and fatty
acids it has not been possible hitherto to get a satisfactory
value for the characteristic OH group, but if provisionally we
take 1·3 as the increase of $(M_2{}^2l_2)^{\frac{1}{2}}$, when H is replaced by
OH, then we can obtain values of $(M_2{}^2l^2)^{\frac{1}{2}}$ in the following
manner. For oxalic acid $(COOH)_2$ we start from C_2H_6 with

a value $2 \times \cdot9$ for $2CH_2$, and $2\cdot2$ for the two terminal H atoms, COO has a value $1\cdot8$, as against $\cdot9$ for each CH_2 group; so that if the allowance to be made for displacing a terminal H from a paraffin and attaching it to O in OH is small, as it probably is, then the value for $(COOH)_2$ will be about $1\cdot8 + 2\cdot2 + 1\cdot8$, that is $5\cdot8$: so for citric acid $C_3H_4OH(COOH)_3$, if we start from C_3H_8 with the value $3 \times \cdot9 + 2\cdot2$ we have to add $3 \times 1\cdot8$ for the substitution of COOH for H three times, and $1\cdot3$ for the substitution of OH for H, giving a total of $11\cdot6$; so for glycerine $C_3H_5(OH)_3$ the value of C_3H_8 is $4\cdot9$, and three substitutions of OH for H cause an addition of $3\cdot9$, yielding the total $8\cdot8$; so for tartaric acid $C_2H_2(COOH)_2(OH)_2$ the value is $4 + 3\cdot6 + 2\cdot6$, that is $10\cdot2$.   Mannite $C_6H_8(OH)_6$ and dextrose $C_6H_6(OH)_6$ will have practically the same value for $(M_2{}^2l_2)^{\frac12}$, because the olefines have the same values as the paraffins; for C_6H_{14} the value is $6 \times \cdot9 + 2\cdot2$, and six substitutions of OH for H mean an increase of $7\cdot8$, so that the total for mannite and dextrose is $15\cdot4$.   In the case of cane-sugar $C_{12}H_{22}O_{11}$, if we start from $C_{12}H_{24}$ with a value $12 \times \cdot9 + 2\cdot2$, after adding $14\cdot3$ for 11 substitutions of OH for H we shall have to subtract a certain amount for the two surplus H atoms; this amount is unknown, and as being probably small may be neglected, so that for $C_{12}H_{22}O_{11}$ we have $27\cdot3$.

As a preliminary examination showed that the following compounds have the same value for

$$c(\rho_1/\alpha_1{}^{\frac13})M_2(M_2/\rho_2)^{-\frac16} \div (M_2{}^2l_2)^{\frac12}$$

as the metallic compounds of type NaCl, the equation used for calculating c is (10), in which, according to Traube's measurements, α_1 has the value $7\cdot385$.

Table X.

	Oxalic acid.	Citric acid.	Glycerine.	Tartaric acid.
p_2	$\cdot069$	$\cdot17$	$\cdot19$	$\cdot184$
ρ	$1\cdot0337$	$1\cdot0749$	$1\cdot0403$	$1\cdot0916$
a	$7\cdot307$	$7\cdot067$	$7\cdot300$	$7\cdot413$
$_1A_2a_2{}^{\frac13}/\rho_2(_1A_1\,_2A_2)^{\frac13}$ ...	$1\cdot21$	$1\cdot16$	$1\cdot82$	$1\cdot36$
$(M_2{}^2l_2)^{\frac12}$	$5\cdot8$	$11\cdot6$	$8\cdot8$	$10\cdot2$
	$7\cdot4$	$7\cdot5$	$9\cdot6$	$7\cdot8$

	Mannite.	Dextrose.	Cane-sugar.
p_2	$\cdot097$	$\cdot171$	$\cdot186$
ρ	$1\cdot0342$	$1\cdot0660$	$1\cdot0778$
a	$7\cdot443$	$7\cdot506$	$7\cdot478$
$_1A_2a_2{}^{\frac13}/\rho_2(_1A_1\,_2A_2)^{\frac13}$ ...	$1\cdot76$	$1\cdot66$	$1\cdot56$
$(M_2{}^2l_2)^{\frac12}$	$15\cdot4$	$15\cdot4$	$27\cdot3$
	$9\cdot1$	$8\cdot1$	$7\cdot3$

The mean value of $c(\rho_1/\alpha_1^{\frac{1}{2}})M_2(M_2/\rho_2)^{-\frac{1}{6}} \div (M_2^2 l_2)^{\frac{1}{2}}$ for these compounds is 8·1, which is not far from the 8·5 found for the inorganic compounds of types NaCl and MgCl$_2$.

Some transition cases between organic and inorganic compounds can be studied by means of some data of Traube's for formates and acetates of Na, Ca, and Ba, for which we can calculate the values for $(M_2^2 l_2)^{\frac{1}{2}}$ by using 2·9 for HCOO and 3·8 for CH$_3$COO, and 3·5 for Na, remembering that in the case of the dyad metals $(M_2^2 l_2)^{\frac{1}{2}}/2^{\frac{1}{2}}$ for the formates and acetates is found by adding the values just given for HCOO and CH$_3$COO to 3·2 for Ca and 4·2 for Ba.

TABLE XI.

	Na Form.	Na Ac.	Ca Form.	Ca Ac.	Ba Form.	Ba Ac.
p_2	·075	·058	·094	·086	·079	·088
ρ	1·0598	1·0309	1·0664	1·0505	1·0815	1·0677
a	7·577	7·486	7·491	7·363	7·523	7·392
$_1A_2\alpha_2^{\frac{1}{2}}/\rho_2(_1A_{1\,2}A_2)^{\frac{1}{2}}$	1·19	1·56	1·08	1·11	·42	·72
$(M_2^2 l_2)^{\frac{1}{2}}$	6·4	7·3	8·5	9·8	9·9	11·2
	7·0	9·0	8·2	8·3	4·7	7·6

Here again the value of the ratio, except for Ba Form., is not far from the 8·1 just found for organic compounds, or the 8·5 for inorganic of the types NaCl and MgCl$_2$.

The general result may, therefore, be stated that a value of $_1A_2\alpha_2^{\frac{1}{2}}/\rho_2(_1A_{1\,2}A_2)^{\frac{1}{2}}$ for water and a compound of a monad metal with a monobasic acid, or for water and an organic compound, can be got from the surface-tension of a dilute aqueous solution according to the equation (10); for water and a compound of a monad metal with a dibasic acid according to (11) ; and for water and a compound of a dyad metal with a monobasic acid according to (12) ; and that then from this a value of $(M_2^2 l_2)^{\frac{1}{2}}$ for the dissolved substance can be got by the equations

$$(M_2^2 l_2)^{\frac{1}{2}} = {}_1A_2 M_2(M_2/\rho_2)^{-\frac{1}{6}}\alpha_2^{\frac{1}{2}}/\rho_2\, 8·5\, (_1A_{1\,2}A_2)^{\frac{1}{2}} \Big\}.\quad (13)$$
$$\text{for the types NaCl and MgCl}_2$$

$$(M_2^2 l_2)^{\frac{1}{2}} = {}_1A_2(M_2/\rho_2)^{\frac{5}{6}}\alpha_2^{\frac{1}{2}}/4·4\, (_1A_{1\,2}A_2)^{\frac{1}{2}} \Big\};\quad (14)$$
$$\text{for the type K}_2\text{SO}_4$$

to organic compounds we cannot say which of these forms applies.

Now we formerly took $_1A_2/(_1A_{1\,2}A_2)^{\frac{1}{2}}$ as being given provisionally by 7·25/13 for the type NaCl, but in harmony with the majority of our data this should be 8·5/13 or ·65, and for

the type $MgCl_2$ in place of our former $7\cdot25/19$ we should take $8\cdot5/19$ or $\cdot45$, and for the type K_2SO_4 $4\cdot4/19$ or $\cdot23$; thus for the type NaCl we have the equation

$$(M_2{}^2 l_2)^{\frac{1}{2}} = \alpha_2{}^{\frac{1}{2}}(M_2/\rho_2)^5/13 = \cdot 08\,\alpha_2{}^{\frac{1}{2}}(M_2/\rho_2)^{\frac{5}{6}}, \quad . \quad (16)$$

and for the types $MgCl_2$ and K_2SO_4 the equation

$$(M_2{}^2 l_2)^{\frac{1}{2}} = \alpha_2{}^{\frac{1}{2}}(M_2/\rho_2)^{\frac{5}{6}}/19 = \cdot 05\,\alpha_2{}^{\frac{1}{2}}(M_2/\rho_2)^{\frac{5}{6}}. \quad . \quad (17)$$

Now for the three types we ought to have the same equation, for the fundamental equation for giving a value of $(M_2{}^2 l_2)^{\frac{1}{2}}$ from a value of α_2 measured at $\frac{2}{3}$ of the critical temperature is (" Laws of Molecular Force," Phil. Mag. 5 ser. xxxv. p. 258), in terms of 10^{12} dynes as unit of force which has been used throughout my values of $M^2 l$,

$$(M_2{}^2 l_2)^{\frac{1}{2}} = \cdot 109\,\alpha_2{}^{\frac{1}{2}}(M_2/\rho_2)^{\frac{5}{6}}; \quad . \quad . \quad . \quad (17)$$

or if α_2 is measured at the melting-point a rougher approximation to the truth is (" Further Studies," Phil. Mag. Jan. 1895)

$$(M_2{}^2 l_2)^{\frac{1}{2}} = \cdot 097\,\alpha_2{}^{\frac{1}{2}}(M_2/\rho_2)^{\frac{5}{6}}. \quad . \quad . \quad . \quad (18)$$

Thus the difference in the equations (15) and (16) above is probably due to some fact not taken account of in interpreting b for all the types as being $\alpha_2/\rho_2{}^2$; the difference would be explained if $b^{\frac{1}{2}}$ for the type NaCl were too small in the ratio of 13 to 19, or in the types $MgCl_2$, K_2SO_4 too large in the ratio of 19 to 13; that is, if b were too small in the ratio of 1 to $2\cdot1$ in the one case, or too large in the ratio $2\cdot1$ to 1 in the other: in round numbers we have to do with an unexplained factor 2 or $\frac{1}{2}$ in one case or the other.

Let us now compare the equations (15) and (16) with (17) and (18); the coefficients $\cdot08$ and $\cdot05$ are smaller than the $\cdot109$ and $\cdot097$, because α_2, being measured at the much lower temperature of $15°$ C., is larger, for the lower the temperature the smaller must the coefficient be. We can determine approximately whether the difference in the coefficients really corresponds to the difference in temperature, for according to the discovery of Eötvös (Wied. *Ann.* xxvii.), confirmed by Ramsay and Shields, the change in $\alpha_2(M_2/\rho_2)^{\frac{2}{3}}$ for 1 degree C. change of temperature is nearly $\cdot227$ for all normal liquids; and if we extend this principle into the solid state for, say, NaCl, whose absolute melting-point is 1045, then at $15°$ C. or $288°$ absolute $\alpha_2(M_2/\rho_2)^{\frac{2}{3}}$ increases by $\cdot227 \times 757$ above what it is at the melting-point; but at the melting-point α_2 is $11\cdot6$ according to Quincke and Traube, and at the melting-

point ρ_2 according to Quincke is 2·04, while at 15° C. it is
2·09. Thus all the data are to hand for calculating α_2 at 15°
C., it comes out 30·5 ; now $(30·5/11·6)^{\frac{1}{2}}$ is 1·62, which ought
to be the ratio of the coefficient in (18) to that in (16). If we
divide ·097 in (16) by 1·62 we get ·06 in place of the ·08 of
(15) or the ·05 of (16), which shows that in a general way
the magnitudes of our quantities calculated from solutions at
15° C. agree with their values calculated for the pure sub-
stances at their high melting-points.

We can now illustrate the determination of $(M_2{}^2 l_2)^{\frac{1}{2}}$ for a
substance by a measurement of the surface-tension of a solu-
tion of it in the cases of $AgNO_3$, $Pb(NO_3)_2$, and $MnCl_2$, for
which Valson's data are available ; first by (10) for $AgNO_3$,
and by (12) for $Pb(NO_3)$ and $MnCl_2$ we calculate

$$ {}_1A_2\alpha_2^{\frac{1}{2}}/\rho_2({}_1A_{1\ 2}A_2)^{\frac{1}{2}}, $$

and then by (13) and (14) obtain $(M_2{}^2 l_2)^{\frac{1}{2}}$ with the following
results :—

<div align="center">

TABLE XII.

</div>

	$AgNO_3$.	$Pb(NO_3)_2$.	$MnCl_2$.
p_2	·145	·142	·060
ρ	1·133	1·133	1·052
α	7·575	7·546	7·551
${}_1A_2\alpha_2^{\frac{1}{2}}/\rho_2({}_1A_{1\ 2}A_2)^{\frac{1}{2}}$......	·611	·515	·705
M_2/ρ_2	39	68	42
$(M_2{}^2 l_2)^{\frac{1}{2}}$	6·6	10·0	5·6

According to the Kinetic Theory of Solids (" Further
Studies," p. 27) $(M_2{}^2 l_2)^{\frac{1}{2}}$ for $AgNO_3$ is 7·0 as against the 6·6
just found ; with 3·6 as the value for NO_3, 6·6 would mean a
value 3·0 for Ag, while from the chloride (" Further Studies,"
p. 22) the value is 2·9, from the bromide 2·7, and from the
iodide 3·3. According to the principles explained in " Further
Studies," the value of $(M_2{}^2 l_2)^{\frac{1}{2}}$ for $Pb(NO_3)_2$ must be divided
by $2^{\frac{1}{2}}$, giving 7·1, which is the sum of 3·6 for NO_3, and a
part due to Pb, which must therefore be 3·5 ; according to
the data of " Further Studies," p. 22, the part due to Pb is 3·1
from the chloride, 3·0 from the bromide, and 2·7 from the
iodide ; on dividing the 5·6 for $MnCl_2$ by $2^{\frac{1}{2}}$ and subtracting
2·1 for Cl, we have the part 1·9 due to Mn.

It has been shown that the attracting powers of the mole-
cules of solid bodies can be determined by measuring the
surface-tension and density of solutions of known strength,
and that the values so found agree in the main with those
obtained by measurements of the surface-tensions of the

substances at their melting-points, and with those obtained according to the Kinetic Theory of Solids; there remains now to discuss the meaning of a peculiar empirical relation given in "The Laws of Molecular Force" (Phil. Mag. 5 ser. xxxv. p. 277), namely, that if w is the molecular mass of water, and p the molecular mass of a substance dissolved in it to form a solution containing n molecules of p to 1 of w, then the solution may be regarded as a substance of molecular mass $m=(w+np)/(1+n)$, these molecules m attracting one another according to the law $3Xm^2/r^4$, so that X can be calculated from the surface-tension of the solution according to the equation

$$\alpha = kX\rho^{\frac{5}{3}}m^{\frac{1}{3}}.$$

Then it was asserted that W in $3Ww^2/r^4$ for the attraction of two molecules of water, and A in $3Ap^2/r^4$ for the attraction of two molecules of the dissolved substance, are connected with X by the peculiar relation

$$X^{-1}(W^{-1}+nA^{-1})/(1+n),$$

so that A^{-1} can be calculated from the observed surface-tension of the solution. As they stand, these equations can be got to represent the connexion between surface-tension and concentration in solutions fairly well, and by slight modification can be got to represent the relation accurately; but from the previous part of this paper it can be seen that they can only do so in an accidental empirical manner, for $X^{-1}+(X^{-1}-W^{-1})/n$, which in our empirical relation is assumed to be A^{-1}, can be expressed in a form which shows it to be a function of p and A, approximately linear in each; it so happened that for a number of organic compounds this function was approximately equal to A^{-1}, and was therefore identified as such, but with the values found in this paper for $(M_2^2l_2)^{\frac{1}{2}}$, which is proportional to $A^{\frac{1}{2}}M$, it appears that for the inorganic compounds the function cannot be said to be equal to A^{-1}, unless in a very roughly approximate manner. Thus all that was said in sections 15 and 16 of "The Laws of Molecular Force," on the supposition that what was denoted by A^{-1} was really A^{-1}, must be withdrawn to be replaced by the results of the present paper. The relation which was proved in the former paper to hold between the surface-tensions and compressibilities of solutions can be brought out more clearly when we abandon the empirical relation and proceed according to dynamical principles. We have to establish a relation between the compressibility μ and l,

which has been done for normal liquids on p. 241 of " The Laws of Molecular Force," the result being that l is approximately proportional to $aT/\mu\rho^2$, where a is the coefficient of expansion, and T is the absolute temperature ; and in " A Kinetic Theory of Solids " (Phil. Mag. 5 ser. xxxii. pp. 530, 531) it is shown that $1/\mu$, there denoted by k, is approximately proportional to an expression which is equal to $l\rho^2$ divided by aT. Thus both for normal liquids and solids l is proportional to $aT/\mu\rho^2$; so that in spite of the abnormality of water and solutions we are entitled for comparative purposes to assume a similar form of relation with the additional assumption that as aT represents the ratio of the space free of matter to the space occupied by the molecules, it may be taken to be the same for solutions (especially dilute ones) as for water, so that for water and solutions at a given temperature l is approximately proportional to $1/\mu\rho^2$. Now $l\rho^2$ represents the attraction exerted by the matter on one side of a plane on a cylinder on the other side which stands normally on unit area in the plane. If the matter consists of p_1 parts of 1, and p_2 parts of 2, forming a gramme of mixture of density ρ, then the density of the p_1 gramme distributed through a space $1/\rho$ is $p_1\rho$, and the attraction due to molecules of 1 on opposite sides of the plane is $l_1 p_1^2\rho^2$, so for the molecules of 2 it is $l_2 p_2^2\rho^2$, and for the mutual attractions of 1 and 2 it is

$$2_1A_2(l_1 l_2)^{\frac{1}{2}}p_1 p_2\rho^2/(_1A_1{_2}A_2)^{\frac{1}{2}},$$

so that

$$l=p_1^2 l_1 + \frac{2_1A_2}{(_1A_1{_2}A_2)^{\frac{1}{2}}}p_1 p_2(l_1 l_2)^{\frac{1}{2}} + p_2^2 l_2, \quad . \quad . \quad (19)$$

and if $l=c/\mu\rho^2$, $l_1=c/\mu_1\rho_1^2$, then

$$\frac{1}{\mu\rho^2} = \frac{p_1^2}{\mu_1\rho_1^2} + \frac{2_1A_2}{(_1A_1{_2}A_2)^{\frac{1}{2}}}\frac{p_1 p_2(l_2/c)^{\frac{1}{2}}}{(\mu_1\rho_1^2)^{\frac{1}{2}}} + p_2^2 l_2/c, \quad . \quad (20)$$

which is the law connecting the compressibility of a solution with its concentration and with the properties of its components ; remembering that $p_1=1-p_2$, this becomes

$$\frac{1}{\mu\rho^2} - \frac{1}{\mu_1\rho_1^2} = 2p_2\left\{ \frac{_1A_2}{(_1A_1{_2}A_2)^{\frac{1}{2}}}\left(\frac{l_2/c}{\mu_1\rho_1^2}\right)^{\frac{1}{2}} - \frac{1}{\mu_1\rho_1^2} \right\}$$
$$+ \text{ a term in } p_2^2; \quad . \quad (21)$$

for dilute solutions the term in p_2^2 can be neglected. We can illustrate the truth of this *form* of relation by applying it

to Röntgen and Schneider's results for compounds of Na (Wied. *Ann.* xxix.).

<div align="center">TABLE XIII.</div>

	NaCl.	NaBr.	NaI.	NaNO$_3$.	Na$_2$CO$_3$.
p_2	·083	·134	·187	·114	·138
ρ.........	1·058	1·112	1·165	1·079	1·146
$10^7\mu$ ...	394	401	405	402	304
p_2	·040	·069	·095	·057	·069
ρ.........	1·028	1·054	1·078	1·038	1·071
$10^7\mu$ ...	429	432	434	432	377

These measurements were made at temperatures near 18° C., at which $10^7\mu_1$ for water is 467, and they give the following values of $10^{-2}(1/\mu\rho^2 - 1/\mu_1\rho_1{}^2)/p_2$:—

NaCl.	NaBr.	NaI	NaNO$_3$.	Na$_2$CO$_3$.
157	−89	−171	0	261
148	−87	−168	18	245

Similar results are given by their data for the compounds of Li and K. The data of M. Schumann (Wied. *Ann.* xxxi.) show what he calls anomalies at very low concentrations, and at these strengths do not satisfy the equation ; but at the higher strengths his results are in accord with the equation, so that probably there is some source of experimental error which is responsible for the seeming anomalies, and accordingly in using Schumann's data below for CaCl$_2$, SrCl$_2$, and BaCl$_2$ only those solutions in which p_2 is greater than ·1 have been employed.

To the values of $(1/\mu\rho^2 + 1/\mu_1\rho_1{}^2)/p_2$ we have only to add $2/\mu_1\rho_1{}^2$ to get quantities proportional to $_1A_2 l_2{}^{\frac{1}{2}}/(_1A_{1\,2}A_2)^{\frac{1}{3}}$, and if $_1A_2/(_1A_{1\,2}A_2)^{\frac{1}{2}}$ is constant, these values multiplied by M_2, the molecular mass of the dissolved substance referred to the H atom, must yield quantities proportional to $(M_2{}^2 l_2)^{\frac{1}{3}}$. The following table contains the values of

$$10^{-2}\{(1/\mu\rho^2 - 1/\mu_1\rho_1{}^2)/p_2 + 2/\mu_1\rho_1{}^2\},$$

and its ratio to $(M_2{}^2 l_2)^{\frac{1}{2}}10^2$ for compounds of Li, Na, and K from Röntgen and Schneider's data, and for the chlorides of Ca, Sr, and Ba from Schumann's at 15° C., his value of $10^7\mu_1$ for water being 464. The values of $(M_2{}^2 l_2)^{\frac{1}{2}}$ are given in previous tables in this paper.

Table XIV.

$LiCl$.	$LiBr$.	LiI.	$LiNO_3$.	Li_2SO_4.	$NaCl$.	$NaBr$.
713	368	254	486	673	· 581	340
67	63	56	56	72	61	56

NaI.	$NaNO_3$.	Na_2SO_4.	Na_2CO_3.	KCl.	KBr.	KI.
258	437	516	681	500	331	256
54	52	66	82	56	54	51

KNO_3.	K_2SO_4.	K_2CO_3.	$CaCl_2$.	$SrCl_2$.	$BaCl_2$.
383	478	564	400	330	272
47	66	72	56	60	60

The ratios in the second row have values between 47 and 82, and in each series they diminish in the order carbonate, sulphate, chloride, bromide, iodide, and nitrate; and although the compounds of the dibasic acids do not separate themselves from the others by any distinct gap, yet if on account of what we have seen in connexion with surface-tension we set them apart, the ratios for the rest lie between 47 and 67 with a mean value 57, which is close to the value for 12 out of 15 of the compounds; or, in other words, the relative values of $(M_2{}^2 l_2)^{\frac{1}{2}}$, calculated on dynamical principles from the experimental compressibilities of solutions, agree within the limits of experimental error with the relative values given by the Kinetic Theory of Solids for 12 out of 15 substances of the types $NaCl$ and $MgCl_2$.

For the five values of compounds with dibasic acids, the mean is 72, which is larger than the 57 for the other compounds, a result in striking contrast to that of Table VII., where the corresponding ratio in connexion with surface-tensions came out for compounds with the dibasic acids only half of the value for other compounds. This discrepancy shows that the equation (21) is not a complete statement of the facts of the compressibility of solutions; instead of saying that $(1/\mu\rho^2 - 1/\mu_1\rho_1{}^2)p_2 + 2/\mu_1\rho_1{}^2$ is equal to $2_1 A_2 (l_2 / c\mu_1\rho_1{}^2)^{\frac{1}{2}} / (_1 A_1{}_2 A_2)^{\frac{1}{2}}$ we should say that amongst compounds of the types $NaCl$ and $MgCl_2$ it is proportional to it, and also in the type Na_2CO_3 it is proportional to it, but with a different factor of proportionality. We can see that this is true in another way, because if equation (21) were strictly correct then $10^{-4} M_1 / \mu_1\rho_1{}^2 (M_1{}^2 l_1)^{\frac{1}{2}}$ for water ought to have a value differing from that of the ratios above by the factor $2_1 A_2 / (_1 A_1{}_2 A_2)^{\frac{1}{2}}$, which we have seen from surface-tensions cannot be much different from 1; now $(M_1{}^2 l_1)^{\frac{1}{2}}$ for water being about 2·4, $10^{-4} M_1 / \mu_1\rho_1{}^2 (M_1{}^2 l_1)^{\frac{1}{2}} = 16$, which is only about a quarter of

the averages 57 and 72 found above. The reason for this state of affairs lies probably in the fact that when salts are dissolved in water there is a shrinkage which probably implies a considerable compression of the water and an alteration of its compressibility, so that μ_1 cannot be taken to have the value found in pure water at low pressures ; from what has gone before it would appear that the alteration of μ_1 is proportional to $(M_2{}^2 l_2)^{\frac{1}{2}}$ amongst compounds of the same type. It is evident that the compressibility of solutions has been merely touched on here, and that a complete treatment of the subject would demand a knowledge of the characteristic equation for water. The little that has been written here has been brought forward to indicate that there are simple principles on which a preliminary exploration can be carried on.

The chief result of the present paper is to show that the surface-tension of aqueous solutions follows the same laws as the surface-tension of mixed liquids, except that the ratio ${}_1A_2/({}_1A_1\, {}_2A_2)^{\frac{1}{2}}$ does not appear to have the value 1 characteristic of most mixtures of two liquids, though it has the same value for all compounds of the same chemical type ; it has also been shown that the values for molecular attraction obtained from the surface-tensions of solutions agree with those obtained according to the Kinetic Theory of Solids.

Melbourne, March 1895.

XLV. *Galvanometer Design.   Waste Space near the Needle.*
    By Professor S. W. HOLMAN [*].

IN this Magazine for July 1890, Messrs. Ayrton, Mather, and Sumpner gave a demonstration to show that in the coil of a sensitive (Thomson) galvanometer the current in a portion of the central turns affected the needle in opposition to the remaining major part of the turns ; so that this portion should be left out or connected in reversed direction. The space containing these turns was pointed out as being nearly " an oblate spheroid with a polar axis about 0·72 of its equatorial diameter, the latter being of course slightly larger than the length of the needle " (p. 65).

This point which, if correct, would be of practical significance, becomes less important from the fact that in the ordinary construction much of this particular volume must be left empty for the insertion and free motion of the needle —one reason perhaps why its partial incorrectness has not hitherto been commented upon. Inasmuch, however, as Gray has introduced it into his most valuable ' Absolute

Measurements &c. ' (ii. p. 375), and because of the weight attaching to the names of the authors putting forth the proposition, its emendation seems worth the short space necessary.

Briefly stated, it is true that the turns occupying a small volume near the centre of a solid coil would have a reversed effect upon a needle of finite length, but the volume is roughly from one quarter to one eighth only of that indicated by Ayrton, Mather, and Sumpner. It is approximately a central sphere whose diameter is about one-half the length of the needle, or the equivalent in volume of such a sphere. Thus this consideration *does* become entirely insignificant in practical construction, the major part of such a spherical space being inevitably left empty. The diameter, one-half of $2l$, is but a very rough approximation, first arrived at from a simple qualitative experiment. It would be an instructive and not a difficult task for a student to map out the space experimentally, and to locate the actual bounding-curves for the surfaces of equal efficiency for which Thomson and Maxwell have given the equation relatively to the field at the centre without discussing the effect of a needle not indefinitely short. This work I shall endeavour to have performed.

The error in the demonstration arose from the fallacy of considering the deflective moment upon the needle as due to the intensity and direction of the field at the magnetic poles merely, regardless of the fact that the field over the remainder of the needle is not the same as at the poles either in direction or strength.

Let the dots $a_1\ a_2$ represent the section of the wire of one small turn, the diagram being a horizontal central section. Let $n\,s$ be the needle of length $2l$, the turn thus being one of a diameter much less than $2l$. The deflecting moment due to a current in the coil, assuming a very thin uniformly magnetized prismatic needle, will of course be

$$2 \int_0^l m \,.\, f \cos \theta \,.\, ds,$$

m being the strength of pole of any thin transverse section or shell of the needle, ds the thickness of that section, f the field-intensity at that point, and θ the field-direction angle with the axis of the coil. For the indicated position and any

2 M 2
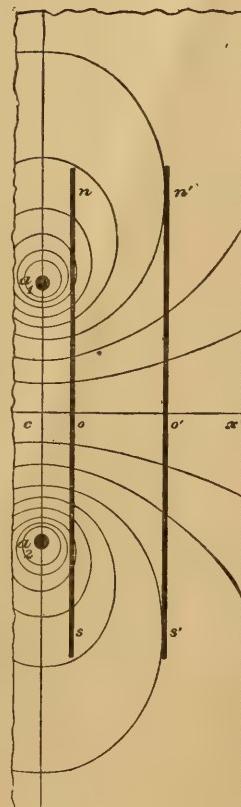
near one, of needle and turn, this integral will be made up of two parts of opposite sign, the change of sign occurring at the point where $\theta = 90°$, *i. e.* where the field is tangent to the needle. Denoting as positive the total moment from the centre to that point, the value of the integral will have the positive sign when this part numerically preponderates, the negative sign when the moment due to the field beyond that point is the greater. The balance will depend on the diameter and distance of the turn relative to the needle-length. For a turn in immediate proximity to the needle, it is obvious that the moment will be nil when *a* is somewhat less than half-way from *o* to *n*, *i. e.*, when the turn-diameter is somewhat less than *l*, half the needle-length. Rough experimental trial confirms this deduction. The further removed the turn is from the needle, the less becomes the negative part of the integral relative to the positive part. Hence the bounding surface for null effect would have a diminishing vertical diameter, and the volume would presumably be not far from that of a sphere of diameter $2l$, as above stated.

In deciding whether it would effect any sensible gain to wind this space and connect it in reverse order, it may be noted that a shell of a thickness of nearly half the radius of the sphere extending from the null surface inward would have almost no effect one way or the other. Moreover, some space immediately about the needle must unavoidably be left vacant. The remaining space would thus be so small that the gain would be almost insignificant. The answer is thus clearly in the negative.

The null bounding surface deduced by Professor Ayrton and others was the locus of the turns whose diameter and distance from the needle were such that the field of each was tangent to the needle at the poles, as it would be for the turn $a_1 a_2$ with the needle at the position $n' s'$. The deflecting moment at this position is not nil but decidedly positive.

As far as it concerns galvanometer design the outcome of the discussion may be put into two sentences :—

1. It is practically useless to wind turns within a distance of about one-quarter of the needle-length of the coil centre :

2. To increase sensitiveness, the needle must be made as short as is consistent with torsion of suspension.

The second inference is, of course, the direct one from Maxwell's formula for the strength of field at the centre in a graded coil, re-enforced by the fact that the use of a finite needle annuls the effect of the otherwise most efficient part of the coil. It means needles much shorter than the customary

one-quarter or three-eighths of an inch, and necessarily, there-fore, of greater effective cross-section.

It may also readily be seen by inspection that a needle of finite length reduces the effectiveness of all the small-diameter turns along the axis of the coils, thus showing that the waste axial space in ordinary constructions is not of such serious amount relatively, but on the other hand further supporting the other arguments for the employment of a very short needle.

In the interest of uniformity of convention this opportunity is taken to urge upon those who describe sensitive galvano-meters, and especially instrument-makers in cataloguing, that they invariably present the data :

d = deflexion in mm. with scale at 1 metre from galvano-meter.

c = current in amperes producing that deflexion.

g = the galvanometer resistance as connected up when d is observed.

t = the time of single swing of the needle when c is measured.

These permit the computation of the several measures of sensitiveness :

$$\frac{d}{c}, \quad \frac{d}{c\sqrt{g}}, \quad \frac{d}{c\sqrt{g}}\frac{10^2}{t^2},$$

so useful in the comparison of instruments, and so essential to an intelligent selection for specific purposes.

Rogers Laboratory of Physics,
Massachusetts Institute of Technology,
Boston, September, 1895.

XLVI. *Note on Tinfoil Grating as a Detector for Electric Waves. By* T. Mizuno, *Rigakushi, Professor of Physics, Daiichi Kōtō Gakkō* * .

1. MUCH interested by Herr E. Aschkinass's experiments described in his paper read before the Physical Society of Berlin, I have been induced to repeat them. How far my results confirm his and how far they differ from them will be seen from this note, in which I also give a few tests of the sensibility of tinfoil grating as a detector of electric

* From a separate impression from the Journal of the College of Science, Imperial University, Tokio, Japan, vol. ix. part 1. Communicated by the Author.

waves, and an account of some experiments to determine the nature of its action.

2. I prepared my gratings by first coating a flat wooden block with tinfoil and then cutting on it a number of fine parallel slits with a sharp knife (see the annexed figure).

A and B are binding screws which are fixed in the block and facilitate the connexion of the grating with a Wheatstone bridge.

The particulars of the two gratings chiefly used in my experiments were as follows :—

    (1) Rectangular in form, 3·5 centim. by 5·1 centim., total number of lines 97, and the resistance nearly 130 ohms.

    (2) Also rectangular, 3·5 centim. by 4·4 centim., the number of lines 118, and the resistance nearly 232 ohms.

3. My primary vibrator was a brass cylinder 3 centim. in diameter and 26 centim. in length, its surface interrupted midway along its length by a spark-gap, and its ends furnished with brass spheres 4 centim. in diameter forming the poles. The wave-length of the electric waves produced was ascertained to be about 60 centim. The vibrator was placed in the focal line of a wooden parabolic cylinder coated inside with tinfoil, whose height was 76 centim., depth 21 centim., and focal length 12 centim. My resonator is very simple in construction and has been found very convenient in my other researches on electric waves. It is merely a rectangular strip of tinfoil, 0·8 centim. in breadth and 60 (30 in some cases) centim. in length, with a gap in the middle, which is so fine that resonance-sparks can easily pass across.

4. I will now describe some experiments (Exp. 1 ... Exp. 6) with the view of showing to what extent metallic gratings can screen the action of electric waves.

Experiment 1.

A wooden board, on which were pasted two parallel tinfoil strips, 33 centim. in length and at a distance of 9·7 centim. from one another, was set up vertically in front of the parabolic cylinder at a distance of about 30 centim. from the vibrator. The grating No. 1 was brought behind the board, and after exposure for about half a minute to electric waves, its resistance was examined by a Wheatstone bridge. The results obtained were as follows :—
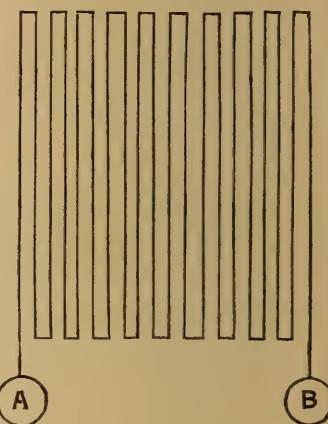
Experiment.	Initial Resistance.	Final Resistance.	Decrease of Resistance.
1.	129·7 ohms.	123·5 ohms.	6·2 ohms.
2.	129·7 ,,	123·4 ,,	6·3 ,,
3.	129·9 ,,	123·6 ,,	6·3 ,,

As Herr Aschkinass mentions, the resistance of the grating once diminished by the action of electric waves could be restored almost to its original value by tapping it. In this experiment, resonance-sparks could be discovered behind the board by means of my tinfoil resonator.

Experiment 2.

Next, a third strip was pasted on the board, half-way between the other two, and the experiment repeated. The results were:—

Experiment.	Initial Resistance.	Final Resistance.	Decrease of Resistance.
1.	129·7	123·7	6·0
2.	129·8	123·8	6·0
3.	130·0	123·5	6·5

Here the resonance-sparks behind the board were very feeble.

Experiment 3.

Two more strips were then added bisecting the spaces between those in the experiment 2.

Experiment.	Initial Resistance.	Final Resistance.	Decrease of Resistance.
1.	129·8	125·8	4·0
2.	129·8	125·6	4·2
3.	130·1	125·7	4·4

The resonator behind the board gave no sparks in this case.

Experiment 4.

Next, a grating, rectangular in form, 27 centim. in length and 22 centim. in breadth, was made, the average distance between two consecutive strips being about 0·6 centim. Placing this grating in a vertical position in front of the parabola and bringing the grating just behind it, the following changes in resistance were observed :—

Experiment.	Initial Resistance.	Final Resistance.	Decrease of Resistance.
1.	129·7	123·7	6·9
2.	129·1	124·1	5·0
3.	129·2	123·5	5·7

Experiment 5.

Substituting for the above grating a large wire grating, 1·7 metre in the side and with consecutive wires 3 centim. apart, I have found the changes of resistance as follows :—

Experiment.	Initial Resistance.	Final Resistance.	Decrease of Resistance.
1.	129·9	126·5	3·4 ‖
2.	129·9	123·4	6·5 ⊥
3.	129·9	126·7	3·2 ‖
4.	130·2	124·5	5·7 ⊥
5.	130·4	127·0	3·4 ‖
6.	130·3	124·1	6·2 ⊥

The signs in the last column of the above table denote the orientations of the wire grating according as the wires were placed parallel or perpendicular to the primary vibrator. The results show how different are the effects of polarized waves on my tinfoil grating. The experiments have shown also how sensitive the tinfoil grating is to the action of electric waves in comparison with my rectilinear tinfoil resonator, because I have found that whereas the former has shown a

large amount of change in resistance the latter gave no perceptible resonance-spark.

Experiment 6.

I have now placed my tinfoil grating within a glass bell-jar which was covered with tinfoil strips. I found that even in this case the change of resistance was distinctly perceptible. Thus :—

Experiment.	Initial Resistance.	Final Resistance.	Decrease of Resistance.
1.	129·7	125·0	4·7
2.	129·9	125·7	4·2
3.	129·9	125·6	4·3

This result may be taken to indicate how imperfect would be the protection of an ordinary metallic gauze against powerful electric oscillations.

Experiment 7.

A circular copper plate 30 centim. in diameter was vertically suspended in front of the vibrator. My tinfoil grating placed behind the plate at a distance of about 12 centim. from it showed the following changes in resistance :—

Experiment.	Initial Resistance.	Final Resistance.	Decrease of Resistance.
1.	129·1	121·0	8·1
2.	129·3	122·3	7·0
3.	129·4	122·0	7·4

Next, the distance between the plate and the grating was diminished to 2·5 centim. The changes were as follows :—

Experiment.	Initial Resistance.	Final Resistance.	Decrease of Resistance.
1.	129·3	123·0	6·3
2.	129·0	123·2	5·8
3.	129·5	123·0	6·5

The difference between the results of this and those of the last experiment I am inclined to ascribe to the diffraction effects of electric waves caused by the plate.

Experiment 8.

A rectangular wooden board, 69 centim. in length and 14 centim. in breadth, was coated all over with tinfoil. When it was held vertically with the longer edges parallel to the primary oscillations, the resistance of my tinfoil grating placed behind it showed no change, but when the edges were placed perpendicular to the primary oscillations, I found :—

Experiment.	Initial Resistance.	Final Resistance.	Decrease of Resistance.
1.	130·0	127·0	3·0
2.	130·8	127·7	3·1
3.	131·4	127·8	3·6

This shows that the intensity of the diffraction effect depends on the extension of the tinfoil board with respect to the direction of the primary oscillations.

Experiment 9.

A parabolic cylinder exactly similar to the one mentioned before was placed against the latter, at a distance of about 1·5 metre, so that their focal lines should be parallel. My tinfoil grating No. 2 was held in the focal line of the second parabolic cylinder and tested ; thus :—

Experiment.	Initial Resistance.	Final Resistance.	Decrease of Resistance.
1.	229·9	219·0	10·9
2.	229·9	219·7	10·2
3.	229·9	219·6	10·3

Taking away the cylinder, I found :—

Experiment.	Initial Resistance.	Final Resistance.	Decrease of Resistance.
1.	230·0	227·6	2·4
2.	230·0	228·0	2·0

Experiment 10.

In this experiment, my tinfoil grating No. 2 was placed just in front of a metallic plate, that is to say, near the node of the stationary electric waves produced by the plate, with the following results : —

Experiment.	Initial Resistance.	Final Resistance.	Decrease of Resistance.
1.	222·0	200·0	22·0
2.	227·0	206·0	21·0
3.	228·0	206·5	21·5

Taking away the plate, I found :—

Experiment.	Initial Resistance.	Final Resistance.	Decrease of Resistance.
1.	227·2	184·7	42·5
2.	225·7	184·5	41·2

Experiment 11.

In order to examine whether the orientation of the tinfoil grating with respect to the primary oscillations has an influence or none on the change of its resistance, the following observations were carried out :—

(1) With the grating No. 1.

Experiment.	Initial Resistance.	Final Resistance.	Decrease of Resistance.	
1.	132·4	125·0	7·4	⊥
2.	132·2	125·5	6·7	‖
3.	132·4	125·2	7·2	⊥
4.	132·4	126·4	6·0	‖
5.	132·5	125·5	7·0	⊥
6.	132·7	126·5	6·2	‖

(2) With the grating No. 2.

Experiment.	Initial Resistance.	Final Resistance.	Decrease of Resistance.	
1.	232·0	189·9	42·1	⊥
2.	232·0	193·0	39·0	‖
3.	232·0	187·0	45·0	⊥
4.	232·0	196·0	36·0	‖
5.	232·4	183·2	49·2	⊥
6.	232·2	194·5	37·7	‖

The signs in the last column indicate the direction of the tinfoil strips of the gratings with respect to that of the primary oscillations. Thus, the answer may be taken as positive.

Experiment 12.

Lastly, I performed some experiments to decide the question whether the change of resistance under consideration is a molecular change as in a selenium cell or simply a mechanical one. For this purpose I prepared very carefully another tinfoil grating with a much wider space between the strips. It was rectangular, 7 centim. in length and 6 centim. in breadth, the total number of fine strips being 51. (See the figure.)
The resistance of the grating thus prepared was 209 ohms.

Now exposing this grating to the action of electric waves, I did not find the least sign of change in its resistance except a very small one due perhaps to the heating effect. The experiment was of course tried several times and also on different occasions, but never with positive result. Here I wish also to notice that although I tried the experiment with fine german-silver wire and also fine iron wire gratings, I could never find any decided effect due to the action of electric waves on them.
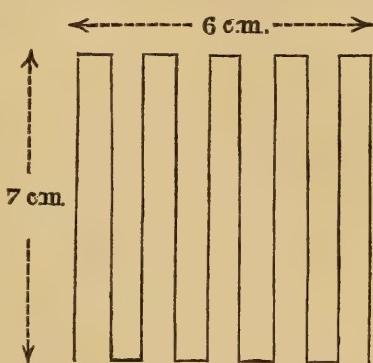
CONCLUSIONS.

I. It is certain that the change of resistance of the tinfoil grating is due to the action of electric waves. So far as the electric discharges in the primary spark-gap are oscillatory, they have an effect on the grating, but if not oscillatory, none.

II. Inasmuch as where my rectilinear tinfoil resonator fails the tinfoil grating shows the presence of electric waves, the latter must be regarded as far more efficient than the former as a detector of electric waves. Even a single spark, if oscillatory, is sufficient to produce a large effect on the grating. I would here call attention to the fact that the change in resistance of one and the same grating observed on different days during the course of my research differed in amount. This is certainly due to the conditions of the spark-gap, and consequently the intensity of the primary oscillations, and also somewhat to the time of exposure.

III. The sensibility of gratings may, up to certain limits, be increased by increasing the fineness and closeness of the strips. For, of my two gratings which are nearly equal in their dimensions but greatly different in the number of strips, the first gave the maximum change of about 6 per cent., while the second gave about 19 per cent.

IV. The phenomenon under consideration may not be molecular, and so far as my experiments go, seems to be purely mechanical. Slits cut in tinfoil with a knife, however sharp they may be, surely have margins which are zigzag. I imagine that the action of electric waves may consist in giving impulses to several strips of tinfoil so as to let the leaflets on

the margins come in contact with one another and thus cause a diminution of the total resistance of the grating. Especially the fact that the spacing of the strips should have so large an influence as to reduce the effect almost to nothing seems to me to favour the above supposition. Also the fact that the change of resistance depends upon the orientation of the strips seems to point in the same direction. Still another fact which is equally important from the above point of view is that the resistance of the tinfoil grating once diminished by an exposure to the action of electric waves can be restored nearly to the original value by tapping the grating. It may be pointed out that Prof. Minchin's experiment * on the action of electromagnetic radiation on films containing metallic powders may stand in close connexion with the present subject.

XLVII. *The Development of Arbitrary Functions.*
By Prof. John Perry *and* Mr. H. F. Hunt†.

STUDENTS at the Finsbury Technical College have for some years carried out the Fourier development idea of the late Professor Clifford by practical Geometrical methods. The curve which graphically represents the function is supposed to be wrapped round a circular cylinder, and the areas of its projections upon two diametral planes enable the coefficients to be found. In 'The Electrician' of June 28th, 1895, one of us gave detailed instructions for carrying out the process. We do not know of any method of development in a Fourier series which can compare with this in either rapidity or accuracy.

In the discussion of Prof. Henrici's paper, April 13th, 1894, one of us described a graphical method of developing any arbitrary function in a series of other normal forms than sines and cosines, such as Bessels or Zonal Spherical Harmonics. It consisted in wrapping the curve which represents the function round a specially shaped cylinder, not circular, and projecting it upon a certain plane. One of us has wasted many months in finding with great exactness a sufficient number of coordinates of the trace of the cylinder suitable for a Zeroth Bessel development. The labour was unnecessary because the coordinate most troublesome to calculate is not really needed : that is, the actual shape of the cylinder is

not needed, and indeed it is better to put aside altogether the idea of a curve being wrapped round a cylinder.

To develop any arbitrary function of x (let us call it y) in normal forms, the real difficulty consists in finding the value of an integral such as $\int_0^a y \cdot Q(x) \cdot dx$, where $Q(x)$ is some tabulated function. If now z is another tabulated function which is the integral of $Q(x)$ the required integral is $\int y \cdot dz$.

Suppose the values of y for 25 equidistant values of x to be known, from $x=0$ to $x=a$ (that is, a is divided into 24 equal parts). Let the corresponding values of z be also tabulated, and let a curve be drawn with the values of y as ordinates and the values of z as abscissæ; the area between this curve and the axis of z gives the value of the integral required.

To illustrate the method we shall show how it is applied in a well-known kind of problem. An arbitrary function $y=f(r)$ of r from $r=0$ to $r=a$ is to be developed in Zeroth Bessels; that is, we must determine the constants A_1, A_2, &c., in

$$f(r) = A_1 J_0(\mu_1 r) + A_2 J_0(\mu_2 r) + \&c. + A_s J_0(\mu_s r) + \&c., \quad (1)$$

where μ_1, μ_2, &c., are the successive roots of

$$J_0(\mu a) = 0. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Now it is well known that

$$A_s = \frac{2}{a^2 [J_1(\mu_s a)]^2} \int_0^a r f(r) J_0(\mu_s r) \cdot dr ; \quad . \quad . \quad (3)$$

or, letting $\mu_s r = x$, (3) becomes

$$A_s = \frac{2}{a^2 [J_1(\mu_s a)]^2} \frac{1}{\mu_s^2} \int_0^{\mu_s a} x f(x) J_0(x) \cdot dx. \quad . \quad (4)$$

Now $\qquad \int x \cdot J_0(x) \cdot dx = x \cdot J_1(x),$

which is easily found for any value of x.

To evaluate the integral in (4), take the 25 equidistant values of our function from 0 to a and use them as the ordinates of points in a curve. The values of the corresponding abscissæ are obtained in the following way. The values of $\mu_1 a$ &c. are the successive roots of $J_0(\mu a) = 0$, and are

$\mu_1 a = 2 \cdot 40483$
$\mu_2 a = 5 \cdot 52008$
$\mu_3 a = 8 \cdot 65373$
$\mu_4 a = 11 \cdot 79153$
and so on.

Take 25 equidistant values of x beginning with 0 and ending with the value $\mu_s a$: the corresponding values of $x J_1(x)$ are the abscissæ of points in the curve required to find A_s.

The area of the curve is easily obtained by means of the planimeter. Having found the 25 abscissæ once for all, they may be used for the development of any arbitrary function of r of which 25 equidistant values are given. We now publish four tables giving these abscissæ, which we have carefully calculated for the first four terms of any such development.

In the column headed P we give the number of the point in the curve of which $x J_1(x)$ is the abscissa, there being 25 such points altogether. In Table I. the point 24 corresponds to $x = 2 \cdot 40483$. In Table II. the point named 24 corresponds to $x = 5 \cdot 52008$, and so on.

In Table II. an additional abscissa is given corresponding to some unknown point between numbers 10 and 11; this is the extreme abscissa of the curve, and the corresponding ordinate would be a tangent to the curve. In Table III. there are two additional or bounding abscissæ and in Table IV. there are three of them.

<table>
<tr><td colspan="2" align="center">TABLE I.</td><td colspan="2" align="center">TABLE II.</td></tr>
<tr><td align="center">P.</td><td align="center">$x \cdot J_1(x)$.</td><td align="center">P.</td><td align="center">$x \cdot J_1(x)$.</td></tr>
<tr><td align="center">0</td><td align="center">0·0000</td><td align="center">0</td><td align="center">0·0000</td></tr>
<tr><td align="center">1</td><td align="center">·0050</td><td align="center">1</td><td align="center">+ ·0267</td></tr>
<tr><td align="center">2</td><td align="center">·0200</td><td align="center">2</td><td align="center">·1010</td></tr>
<tr><td align="center">3</td><td align="center">·0450</td><td align="center">3</td><td align="center">·2242</td></tr>
<tr><td align="center">4</td><td align="center">·0787</td><td align="center">4</td><td align="center">·3800</td></tr>
<tr><td align="center">5</td><td align="center">·1216</td><td align="center">5</td><td align="center">·5578</td></tr>
<tr><td align="center">6</td><td align="center">·1727</td><td align="center">6</td><td align="center">·7458</td></tr>
<tr><td align="center">7</td><td align="center">·2312</td><td align="center">7</td><td align="center">·9191</td></tr>
<tr><td align="center">8</td><td align="center">·2962</td><td align="center">8</td><td align="center">1·0706</td></tr>
<tr><td align="center">9</td><td align="center">·3667</td><td align="center">9</td><td align="center">1·1825</td></tr>
<tr><td align="center">10</td><td align="center">·4416</td><td align="center">10</td><td align="center">1·2417</td></tr>
<tr><td align="center">11</td><td align="center">·5197</td><td align="center">11</td><td align="center">1·2160</td></tr>
<tr><td align="center">12</td><td align="center">·5999</td><td align="center">12</td><td align="center">1·1141</td></tr>
<tr><td align="center">13</td><td align="center">·6807</td><td align="center">13</td><td align="center">·9418</td></tr>
<tr><td align="center">14</td><td align="center">·7609</td><td align="center">14</td><td align="center">·7052</td></tr>
<tr><td align="center">15</td><td align="center">·8392</td><td align="center">15</td><td align="center">·4132</td></tr>
<tr><td align="center">16</td><td align="center">·9142</td><td align="center">16</td><td align="center">+ ·0791</td></tr>
<tr><td align="center">17</td><td align="center">·9845</td><td align="center">17</td><td align="center">− ·2801</td></tr>
<tr><td align="center">18</td><td align="center">1·0490</td><td align="center">18</td><td align="center">·6455</td></tr>
<tr><td align="center">19</td><td align="center">1·1062</td><td align="center">19</td><td align="center">·9963</td></tr>
<tr><td align="center">20</td><td align="center">1·1552</td><td align="center">20</td><td align="center">1·3118</td></tr>
<tr><td align="center">21</td><td align="center">1·1949</td><td align="center">21</td><td align="center">1·5723</td></tr>
<tr><td align="center">22</td><td align="center">1·2242</td><td align="center">22</td><td align="center">1·7605</td></tr>
<tr><td align="center">23</td><td align="center">1·2423</td><td align="center">23</td><td align="center">1·8626</td></tr>
<tr><td align="center">24</td><td align="center">1·2485</td><td align="center">24</td><td align="center">1·8783</td></tr>
<tr><td align="center"></td><td align="center"></td><td align="center">10 A</td><td align="center">1·2485</td></tr>
</table>

TABLE III.

P.	$x \cdot J_1(x)$.
0	0·0000
1	+ ·0640
2	·2434
3	·5036
4	·7921
5	·9485
6	1·2135
7	1·2395
8	1·0986
9	·8366
10	+ ·3353
11	− ·2107
12	·7807
13	1·2957
14	1·6788
15	1·8667
16	1·8195
17	1·5279
18	1·0163
19	− ·3817
20	+ ·4154
21	1·1561
22	1·7807
23	2·2002
24	2·3490
6 A	+1·2485
15 A	−1·8783

TABLE IV.

P.	$x \cdot J_1(x)$.
0	0·0000
1	+ ·1171
2	·4268
3	·8168
4	1·1373
5	1·2468
6	1·0555
7	+ ·5601
8	− ·1542
9	·9246
10	1·5554
11	1·8658
12	1·7443
13	1·1825
14	− ·2851
15	+ ·7485
16	1·6705
17	2·2544
18	2·3065
19	1·8114
20	+ ·8497
21	− ·3674
22	1·5548
23	2·4214
24	2·7410
4 A	+1·2485
10 A	−1·8783
17 A	+2·3490

As an example we have taken a function which has the value 1 at the centre of a circle and the value 0 at the circumference, and which at any place is a linear function of the radius. The outer radius a of the circle is 1.

In fig. 1 the function is shown graphically by the straight line MDD, and the numbered points in this line correspond to 25 equidistant ordinates. In our actual drawing, of which fig. 1 is a reduction, the scale is such that one unit of value of the function corresponds to 10 inches.

The distances from 0 to any number in the axis of abscissæ ON represented in inches ten times the corresponding values of $xJ_1(x)$ of Table I. Projecting vertically from any point in ON, and horizontally from the corresponding point in DD we obtained points in the curve MBB. We use inches because British planimeters usually measure areas in square inches. We found the area OMBBNO to be 61·17 square inches, and as both coordinates were magnified ten times, the

Fig. 1.
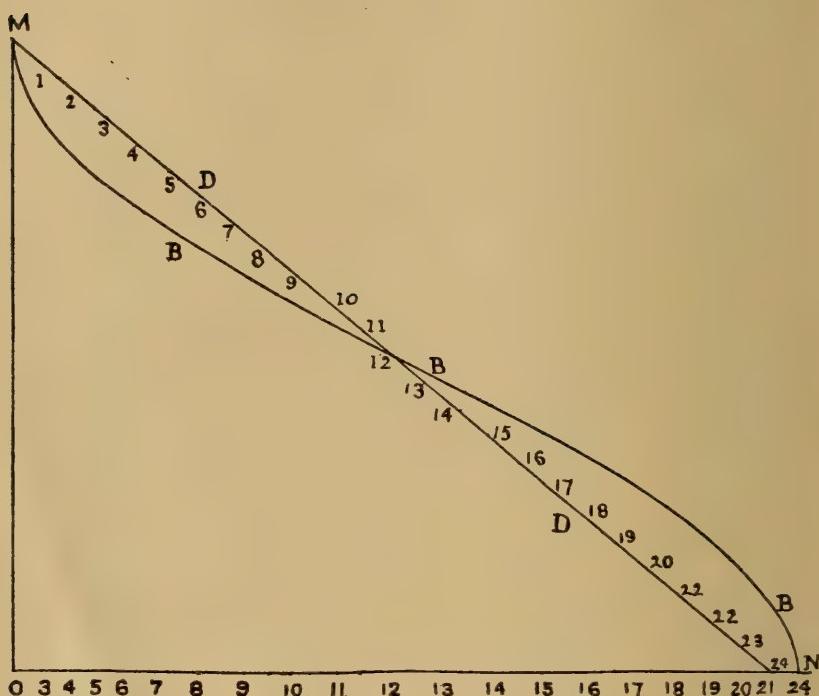
Fig. 2.
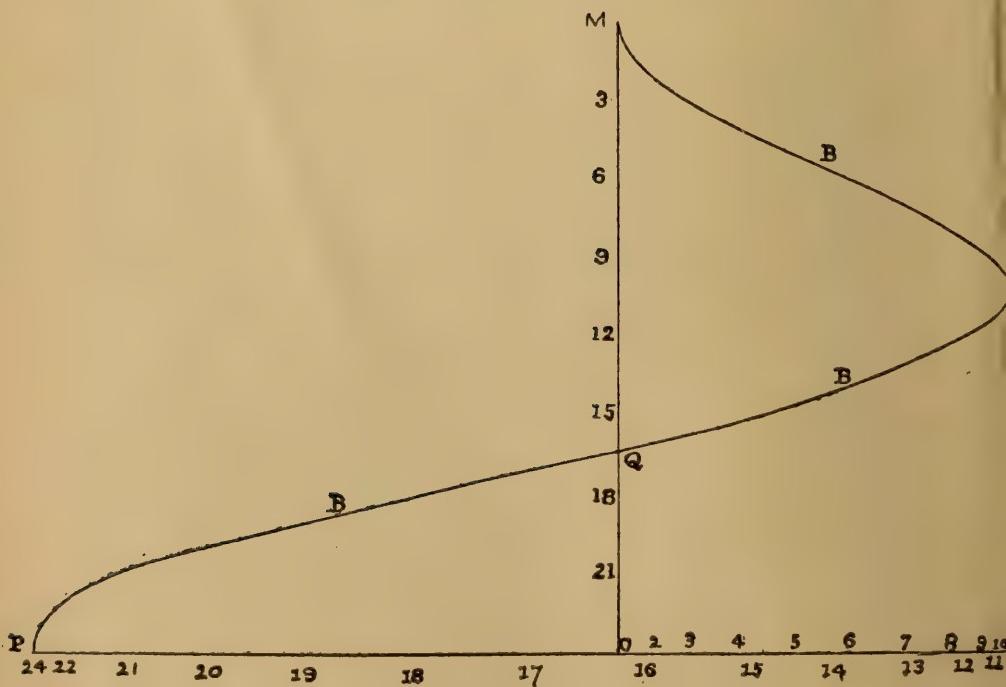
value of the integral in (4) or

$$\int_0^{2\cdot40483} x f(x) \; J_0(x) \, . \, dx = 0\cdot6117,$$

and hence by (4), as $J_1(2\cdot40483) = 0\cdot519$,

$$A_1 = \frac{2 \times 0\cdot6117}{(0\cdot519)^2 (2\cdot405)^2} = 0\cdot7852.$$

To find A_2. The 25 equidistant ordinates of the original curve (straight line) are the ordinates of points in the curve MBLBBP (fig. 2), the abscissæ being taken from Table II. We found it convenient to multiply the abscissæ by 5 and represent in inches. Our ordinates were multiplied by 10 and represented in inches. The actual area was 2·36 square inches and one-fiftieth of this, or 0·0472, is the value of the integral in (4).

Hence, as $J_1(5\cdot5201) = \cdot3403$,

$$A_2 = \frac{2 \times 0\cdot0472}{(0\cdot3403)^2 \times (5\cdot5201)^2} = 0\cdot0268.$$

We need not show the curves used in finding A_3 and A_4. The area of fig. 2 is the positive area MLNOM minus the area LQPNL, but one need not think about whether an area is positive or negative. It is only necessary to start the planimeter-tracer from the point numbered 0 in every case, and go from 0 to M and along the curve in the direction of the increasing numbers to 24, then along the axes of abscissæ, ending at the point 0 from which we started.

XLVIII. *The Relation between the Atom and the Charge of Electricity carried by it. By* J. J. THOMSON, *M.A., F.R.S., Professor of Experimental Physics, Cambridge* *.

IN the electrolysis of solutions, the persistency of the sign of the electric charge carried by an ion is almost as marked a feature as the constancy of the magnitude of the charge. Thus the hydrogen ion always carries a positive charge, the chlorine ion a negative one. In the electrolysis of gases, however, the sign of the charges carried by the atoms of the different elements is much more variable: here an atom of hydrogen does not always carry a positive charge, nor an atom of chlorine always a negative one ; each of these

2 N 2

atoms sometimes carries a negative charge, sometimes a positive one. But though in the gaseous state the atoms do not restrict themselves to charges of one sign, there are many phenomena which prove that even in this state the atoms of the different elements behave differently with respect to positive and negative charges. v. Helmholtz explained this behaviour of the elements by supposing that there is a specific attraction between the atom and its charge ; that the zinc atom, for example, attracts a positive charge more powerfully than it does a negative one, while an atom of chlorine, on the other hand, attracts a negative charge more powerfully than it does a positive one.

The connexion between ordinary matter and the electrical charges on the atom is evidently a matter of fundamental importance, and one which must be closely related to a good many of the most important chemical as well as electrical phenomena. In fact a complete explanation of this connexion would probably go a long way towards establishing a theory of the constitution of matter as well as of the mechanism of the electric field. It seems therefore to be of interest to look on this question from as many points of view as possible, and to consider the consequences which might be expected to follow from any method of explaining, or rather illustrating, the preference which some elements show for one kind of electricity rather than the other.

The following method of regarding the electric field seems to indicate that this effect may be illustrated by simple dynamical appliances. The charges on the atoms are regarded as the ends of Faraday tubes (see J. J. Thomson, ' Recent Researches in Electricity and Magnetism,' p. 2): each unit of positive charge is the origin, each unit of negative charge the termination of such a tube. The magnitude of the unit charge is here taken equal to the charge carried by a monovalent ion. When these tubes spread into the medium they give rise to Maxwell's *Electric Displacement*, and the motion of the tubes through the medium produces a magnetic field.

Now suppose that the medium forming these tubes possesses rotatory motion: we may imagine, for example, that the tubes are bundles of vortex filaments, the axis of rotation being parallel to the axis of the tube. The total amount of vorticity which starts from any solid totally immersed in a liquid is zero ; to satisfy this condition, we may suppose that there is slipping between the walls of the bundle of vortex filaments and the surrounding liquid, or, what amounts to the same thing, that there is on the surface of the bundle a film

of negative vorticity whose strength is equal and opposite to the positive vorticity of the core.   To fix our ideas, let us suppose that the rotation in the core is related to the direction of the axis of the tube (the line running from the origin to the end of the tube) like rotation and translation in a right-handed screw.

Now let us consider the atoms on which these tubes end. Let us suppose that these atoms have a structure possessing similar properties to those which the atoms would possess if they contained a number of gyrostats all spinning in one way round the outwardly drawn normals to their surface.   Then one of these atoms will be differently affected by a Faraday tube, and will possess different amounts of energy according as the tube begins or ends on its surface.   For if, when the tube starts from the atom, the rotation in the core of the tube is in the same direction as the rotation of the gyrostats, then when a tube ends on the atom the rotation in the tube will be in the opposite direction to that of the gyrostats.   Thus in the first case the tube will tend to twist a gyrostat in the same direction as that in which it is already spinning, while in the second case it will tend to twist it in the opposite direction. Now if we try to rotate a gyroscopic system, its behaviour when we try to make it rotate in the direction in which the gyroscopes are spinning is quite different from its behaviour when we try to spin it in the opposite direction.

Thus let fig. 1 represent a balanced gyrostat which can

Fig. 1.
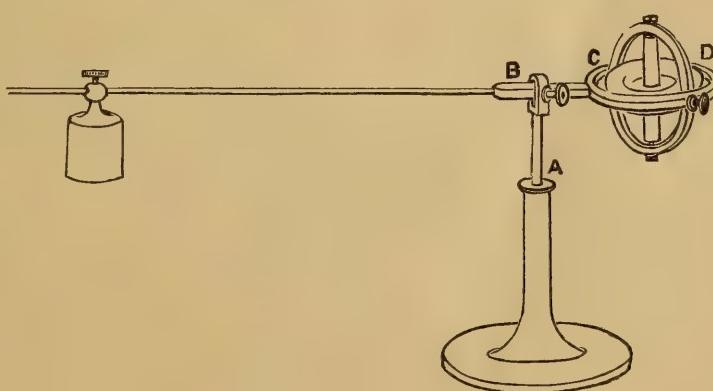
rotate as a whole about the vertical axis A B ; the heavy fly-wheel C D is supported so that its axis can move freely in a vertical plane.   Let this fly-wheel be in rapid rotation with its axis vertical ; the framework of the gyrostat will not tend to rotate.   Now if we set the framework rotating about the

vertical axis, the behaviour of the system, if we make the framework rotate in the direction in which the fly-wheel is spinning, will be very different from its behaviour when we make the framework rotate in the opposite direction.   If the framework rotates in the same direction as the fly-wheel, the axis of the wheel remains vertical, and the whole system goes on rotating quietly until stopped by friction.   If, however, we attempt to set the framework rotating in the opposite direction to the fly-wheel, the axis of the wheel begins to wobble about, the disturbance gets more violent until finally the fly-wheel topples right over ; then the fly-wheel is rotating in the same direction as the framework, and the rotation goes smoothly on.   If the axis of the fly-wheel were held in its original position by springs, then in the first case these springs would not be stretched ; but in the second case they would, and the axis of the fly-wheel would take up a position inclined to the vertical, the angle it made with the vertical depending on the stiffness of the springs and the moment of momentum of the fly-wheel.   Thus in the second case the attempt to make the framework of the gyrostat rotate would be accompanied by the storing up of potential energy in the system due to the stretching of the springs, while there would be no such storage of potential energy in the first case.

Suppose, now, that an atom of hydrogen possesses a structure analogous to this gyroscopic system with springs, the gyrostats rotating in the same direction as the fluid in a Faraday tube *leaving* the atom.   Then, since a charge of negative electricity on the atom implies the *incidence* of a tube on the atom, when the hydrogen atom is charged negatively the rotation in the tube connected with the atom is in the opposite direction to that of its gyrostats.   The negative charge will thus cause an increase in the potential energy of the atom, whereas a positive charge when the rotation in the tube is in the same direction as that of the gyrostats does not cause any such increase.   Thus the internal potential energy of the hydrogen atom will *cæteris paribus* be greater when it has a negative charge than when it has a positive one.   In the case of a strongly electronegative element such as chlorine, we suppose that the gyrostats in the atom are rotating in the opposite direction to those in the hydrogen atom, *i. e.* that in the chlorine atom the rotation in the gyrostats is in the *opposite* direction to that of the liquid in a Faraday tube *leaving* the atom : thus the chlorine atom will, *cæteris paribus*, have more internal potential energy when charged with positive electricity than it has when charged with negative.

The existence of the property conferred by these gyrostats

would call into play forces between two charged atoms placed
very close together, in addition to those given by the ordinary
laws of electrostatics ; it would make, for example, the attrac-
tion between a negatively charged hydrogen atom and a
positively charged chlorine one less than that between a posi-
tive hydrogen atom and a negative chlorine one at the same
distance apart.   For imagine, in the first case, the atoms to
approach a little closer together, then, besides the diminution
in the potential energy due to the ordinary electric forces
between the atoms, there will be an *increase* in the potential
energy from the increase in the effect on the gyrostats due to
the rotation in the Faraday tubes ; while in the second case,
when the hydrogen is positive and the chlorine negative, this
increase will not take place.   Thus the diminution in the
potential energy due to a given diminution in the distance
between the atoms is less in the first case than in the second,
and consequently the attraction between them is smaller in
the first case than in the second.   If we could reach a place
where, as the distance between ths atoms diminished, the in-
crease in the potential energy due to the effect of the gyrostats
was numerically greater than the diminution in the potential
energy due to the electrostatic attraction, then the oppositely-
charged atoms would repel instead of attracting each other.

Hydrodynamical Illustration.

The following illustration also indicates that the force
between two electric charges may be modified by the electro-
chemical properties of the atoms carrying the charges.

In a cylindrical column of rotating fluid the pressure increases
with the distance from the axis of rotation, so that the average
pressure over a cross section of the cylinder is less than the
pressure at the surface of the cylinder.   When a solid is
immersed in a liquid where the pressure is uniform, the pres-
sures of the liquid on the solid form a system of forces in
equilibrium.   Now suppose that a column of the liquid abut-
ting on the solid acquires rotation, the pressure on the part of
the solid in contact with the column will be less than the
pressure outside, the pressures on the solid will no longer be
in equilibrium.   The defect in pressure over the cross section
of the column will give rise to a tension acting on the solid.
This tension is equal to the excess of the pressure over the
cross section, when the pressure is uniform and equal to that
at the surface of the cylinder, over that actually exerted over
the area by the rotating liquid.   If the rotating column is a
cylinder containing a number of vortex filaments mixed up

with irrotationally moving liquid, the pressure over a cross section of the cylinder will depend upon the distribution of the vortex filaments in the cylinder. Let the cylinder be a right circular one. Let v be the velocity, and p the pressure at a distance r from its axis, ρ the density of the liquid; then we have

$$\rho \frac{v^2}{r} = \frac{dp}{dr}. \quad . \quad . \quad . \quad . \quad . \quad (1)$$

The pressure over the cross section of the cylinder is equal to

$$\int_0^b 2\pi r p \, dr,$$

where b is the radius of the cylinder. Integrating this by parts, we find that the pressure Π over the cross section is given by the equation

$$\Pi = P\pi b^2 - \int_0^b \pi r^2 \frac{dp}{dr} \, dr$$

$$= P\pi b^2 - \int_0^b \tfrac{1}{2}\rho v^2 2\pi r \, dr \quad . \quad . \quad . \quad (2)$$

by equation (1), P is the pressure at the surface of the cylinder.
The tension Δ exerted by the cylinder on the solid is given by the equation

$$\Delta = P\pi b^2 - \Pi$$

$$= \int_0^b \tfrac{1}{2}\rho v^2 2\pi r \, dr. \quad . \quad . \quad . \quad . \quad (3)$$

$$= \text{kinetic energy per unit length of the cylinder.} \quad (4)$$

Since

$$2\pi r v = \text{vorticity inside a circle of radius } r,$$

we can, if we know the distribution of vorticity, easily calculate by means of equation (3) the value of Δ.

Let us suppose that if all the vortex filaments were collected round the axis to the exclusion of the irrotationally moving liquid, they would occupy a cylinder of radius a. Let ζ be the rotation in the vortex filament, and let

$$\int_0^b 2\pi r \zeta \, dr = m.$$

Then we find that when the vortex filaments are as close to the axis of the cylinder as possible,

$$\Delta = \frac{\rho m^2}{16\pi} + \frac{\rho m^2}{4\pi} \log \frac{b}{a}.$$

When the vorticity is uniformly distributed over the cross section of the cylinder,

$$\Delta = \frac{\rho m^2}{16\pi}.$$

When the vorticity is all as near to the surface of the cylinder as possible,

$$\Delta = \frac{\rho m^2}{16\pi}\left\{ 1 - 2\frac{(b^2-a^2)}{a^2}\left(1 - \frac{(b^2-a^2)}{a^2}\log\frac{b^2}{b^2-a^2}\right)\right\}.$$

We may expand the right-hand side of the last equation, and get

$$\Delta = \frac{\rho m^2}{8\pi}\left\{ \frac{1}{3}\frac{a^2}{b^2-a^2} - \frac{1}{4}\frac{a^4}{(b^2-a^2)^2} + \frac{1}{5}\frac{a^6}{(b^2-a^2)^3} - \cdots\right\},$$

so that when a is small compared with b,

$$\Delta = \frac{\rho m^2}{24\pi}\frac{a^2}{b^2}.$$

In this case the tension in the cylinder is very small compared with its value in the two previous cases : the value of Δ in the first case is greater than that in the second ; the more the vortex filaments are concentrated at the axis the greater will be the value of Δ. Now let us suppose that a Faraday tube contains a given amount of vorticity distributed among irrotationally moving liquid ; the axes of the vortex filaments being parallel to the axis of the tube. The moment of momentum of the fluid in the tube about its axis will depend upon the distribution of vorticity in the tube : the more the vorticity is concentrated near the axis of the tube the greater will be the moment of the momentum. Now suppose we apply a couple to the Faraday tube, the couple acting in such a direction as to increase the moment of momentum ; this couple will cause the vortex filaments to concentrate more at the axis of the tube, and will consequently increase the tension in the tube. If, however, the couple on the Faraday tube acts in the opposite direction to the moment of momentum of the fluid in the tube, the action of the couple will cause the vortex filaments to spread out and get nearer the boundary of the tube : this will diminish the value of Δ, and consequently diminish the tension in the tube. If we suppose that the solid on which the tube abuts is an atom containing gyrostats, then when the gyrostats are rotating in

the same direction as the fluid in the tube, we may regard the action between the gyrostats and the tube as equivalent to a couple tending to increase the moment of momentum of the fluid in the tube, and thus to increase the pull exerted by the tube on the atom.   When, however, the rotation of the gyrostats is in the opposite direction to that of the fluid in the tube, the action between the atom and the tube will be equivalent to a couple tending to diminish the moment of momentum of the fluid in the tube, and thus to diminish the pull exerted by the tube on the atom.   Thus if, as before, we suppose that the gyrostats in the hydrogen atom are rotating in the same direction as the fluid in the Faraday tube of which it is the origin when it carries a positive charge, whereas the gyrostats in the chlorine atom are rotating in the same direction as the fluid in the Faraday tube of which it is the termination when it carries a negative charge, we see that the attraction between a positively charged hydrogen atom and a negatively charged chlorine one will be greater than that between a negative hydrogen and a positive chlorine atom separated by the same distance.

The object of these illustrations is to call attention to the point that when charged atoms are close together, there may be forces partly electrical, partly chemical, in their origin in addition to those expressed by the ordinary laws of electrostatics.

There are one or two points in connexion with the theory of the electric field which can be illustrated by the conception of a Faraday tube as a bundle of vortex filaments, which, though not connected with the main object of this paper, may be briefly pointed out.   The first of these arises from equation (4), p. 516, which indicates that the tension exerted by a vortex column is equal to the kinetic energy of the fluid in unit length of the column.   Now we know that the forces on a charged body in the electric field are such as would be produced if there were a tension along the lines of force equal per unit area to the electrostatic energy in unit volume of the field.   If we suppose the tension to be exerted by the Faraday tubes and the energy to reside in these tubes, this is equivalent to saying that the tension exerted by each of these tubes is equal to the energy in unit length of the tube.   This exactly coincides with the result indicated by equation (4), if we suppose that the Faraday tubes are bundles of vortex filaments.

The other point is in connexion with the view that magnetic force is due to the movement of the Faraday tubes : the magnetic force being at right angles to the direction of the

Faraday tubes, and also to the direction in which they are moving, the magnitude of the force varying as the product of the "polarization" and the velocity of the tubes at right angles to their direction (see 'Recent Researches in Electricity and Magnetism,' by J. J. Thomson, p. 8). On this view the energy per unit volume in the magnetic field when the tubes are moving at right angles to themselves is (see 'Recent Researches,' p. 9)

$$\frac{\mu}{8\pi} P^2 V^2,$$

where μ is the magnetic permeability, P the polarization, and V the translatory velocity of the tubes. This expression would represent the kinetic energy due to the translatory motion of the tubes if the expression for the effective mass of the tubes contained a term proportional to the square of the "polarization." Now if we have a vortex column moving about in a fluid which is subject to other disturbances, the following considerations would seem to show that the expression for its effective mass would contain a term proportional to the square of the vorticity in the vortex column. The lines of flow when the vortex column is stationary in a

Fig. 2.
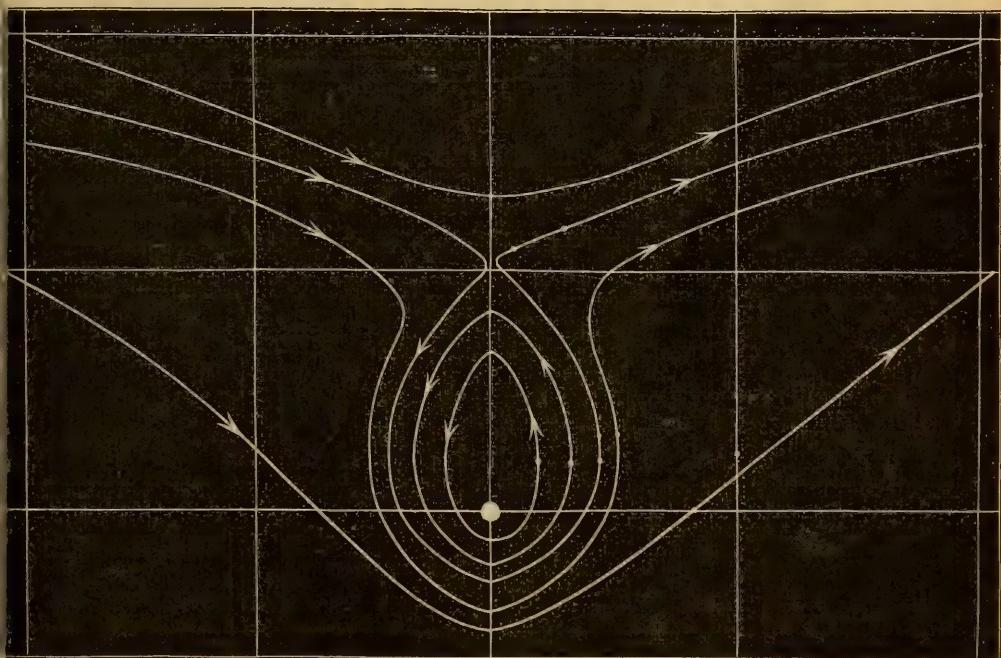
liquid moving so that at an infinite distance its velocity is uniform and horizontal are represented in fig. 2.

We see that some of these lines of flow in the neighbourhood of the column are closed curves ; now the liquid inside any one of these curves will always remain in the neighbourhood of the column, and if the column is moved will move with it : thus the effective mass of the column will be that of the column plus that of the liquid enclosed by the largest of the closed lines of flow. The linear dimensions of the curve are proportional to m/u, where u is the velocity of the fluid at an infinite distance from the column, and m the strength of the vortex ; (the equation to the bounding line of flow is easily seen to be $r = \dfrac{m}{u} e^{-\frac{uy}{m}}$), thus the area enclosed by the line of flow, and consequently the mass of fluid inside a cylinder of which it is the cross section, is proportional to m^2/u^2; thus, as the effective mass is increased by this mass of fluid, the expression for the effective mass of the vortex column will contain a term proportional to the square of the vorticity. Hence, if we regard a Faraday tube as a bundle of vortex filaments, we can by this analogy see that its effective inertia might involve a term proportional to the square of the polarization.

Relation of the preceding Analogies to the Electrochemical Properties of the Atoms.

To return, however, to the relation between the electric charge and the electrochemical properties of the element whose atom carries the charge. The illustration given on page 513 suggests that when an atom is charged with electricity it acquires a certain amount of potential energy depending upon the sign of the charge and also upon the kind of atom carrying the charge. Let us suppose that when an atom of an element A carries unit charge of positive electricity, its potential energy, in consequence of the connexion between the internal motion of the atom and the motion of the fluid in the Faraday tube, is greater by σ_A than when it has no charge, while when the atom has the unit negative charge its potential energy is less by σ_A than that of the uncharged atom. The quantity σ depends upon the nature of the atom ; in 'Recent Researches on Electricity and Magnetism,' p. 64, it is called the Volta potential of the substance, since the difference of potential between two metals A and B when placed in contact can be proved to be equal to $\sigma_A - \sigma_B$.

If the substance A has a charge Q of positive electricity, then in the expression for its potential energy there will be the term $\sigma_A Q$. If we consider this term alone, then if σ_A is positive an increase in the positive charge will involve an

increase in the potential energy, while an increase in the negative charge would diminish the potential energy ; if σ_A is negative the converse is true. Now a dynamical system behaves so as to facilitate any change which causes a diminution in the potential energy. Thus those substances for which σ is negative will tend to acquire a charge of positive electricity, while those for which σ is positive will tend to get a charge of negative electricity. Thus the existence of the property expressed by the coefficient σ would produce the same effect as von Helmholtz's specific attraction of the elements for the two electricities.

Suppose, for example, that we have two metals A and B in contact, and that σ_A, σ_B are the values of the Volta coefficients for A and B respectively; let σ_A be greater than σ_B. Then if A acquires a negative charge equal to $-Q$, and B a positive charge equal to Q, the potential energy of the two metals will be diminished by $(\sigma_A - \sigma_B)Q$. If this were the only source of potential energy, the transference of positive electricity from A to B, and of negative from B to A, would go on indefinitely, as each transference would involve a diminution in the potential energy. The separation of the electricities will, however, produce an electric field the potential energy due to which will increase as Q increases, so that the diminution in energy due to the Volta effect will be accompanied by an increase in the energy due to the electrostatic field. Let us suppose, for example, that the two metals form the plates of a condenser whose capacity is C, then when A has a charge $-Q$ and B a charge $+Q$, the energy in the electrostatic field is equal to

$$\frac{1}{2}\frac{Q^2}{C},$$

while the energy due to the Volta effect is

$$-(\sigma_A - \sigma_B)Q.$$

The flow of negative electricity into A and of positive into B will go on until the increment in the energy of the electrostatic field due to an increase δQ in the charge on B is equal to the decrement of the energy due to the Volta effect produced by the same displacement of electricity.

Since the total energy is

$$\frac{1}{2}\frac{Q^2}{C} - (\sigma_A - \sigma_B)Q,$$

the increment when Q is increased by δQ is equal to

$$\delta Q\left\{\frac{Q}{C}-(\sigma_A-\sigma_B)\right\};$$

or, if V is the difference of potential between A and B, the increment of the potential energy is equal to

$$\delta Q\{V-(\sigma_A-\sigma_B)\}.$$

Thus so long as V is less than $\sigma_A-\sigma_B$, an increase in Q will be accompanied by a decrease in the potential energy, so that Q will tend to increase; while, on the other hand, when V is greater than $\sigma_A-\sigma_B$, an increase in Q will be accompanied by an increase in the potential energy, so that Q will tend to diminish : there will be equilibrium when $V=\sigma_A-\sigma_B$.

We see from this that if an atom of A has a unit negative charge, an atom of B a unit positive one, these atoms will retain their respective charges even though connected by a conductor, unless the potential of B exceeds that of A by more than $\sigma_A-\sigma_B$. If, on the other hand, A had a positive charge, B a negative one, they would, if connected by a conductor, interchange their charges unless the potential of B exceeded that of A by more than $\sigma_A-\sigma_B$.

Thus, assuming that σ is positive for chlorine and negative for hydrogen, an atom of hydrogen could retain a positive charge, and an atom of chlorine a negative one, even though the two were immersed in a conductor, provided the potential of the hydrogen atom did not exceed that of the chlorine atom by more than a certain limit; whereas if the hydrogen were negatively electrified and the chlorine positively, they would, if immersed in a conductor, interchange their charges unless the potential of the hydrogen atom exceeded that of the chlorine by the same limit as before.

Chemical Combination.

Thus, if we have a number of hydrogen atoms and an equal number of chlorine atoms immersed in a conductor, and if initially half of both the hydrogen and chlorine atoms were positively and half negatively electrified, interchange of charges between the atoms would go on until all the hydrogen atoms were positively and all the chlorine atoms negatively electrified.

For this interchange of charges to go on, however, it would seem necessary that a negatively electrified hydrogen atom

and a positively electrified chlorine one should be connected
by a conducting circuit. From the mechanical illustrations
previously given, it seems unlikely that the atoms would inter-
change their charges by coming into contact, the positive
charge passing from the chlorine to the hydrogen atom
and *vice versâ*. From these illus-
trations we should rather expect that if
a negative hydrogen atom came very
near to a positive chlorine one, the two,
if alone in the field, would tend to
repel rather than to attract each other,
the Faraday tube connecting the atoms ceasing to be straight,
and bulging out into the surrounding medium somewhat in
the manner shown in fig. 3.

Fig. 3.

If in addition to the two atoms there were other charged
bodies producing a very intense field tending to push the
hydrogen and chlorine atoms together, then the interchange
of their charges might take place by the ends of the Faraday
tube gliding from one atom to the other after these atoms had
been forced into contact by the external field. There are
indications that the external field would have to be such as to
produce a potential difference of a large number of volts
between the two atoms before this method of exchanging their
charges took place. In the absence of this potential differ-
ence, the atoms would not exchange their charges unless the
medium into which the Faraday tube spread contained some
conductor along which the ends of the Faraday tube could glide
from one atom to the other. The necessity for this conduct-
ing circuit is perhaps one of the reasons why the presence of
a third substance seems necessary for the continuance of
many chemical reactions. How much a third substance able
to act as a conductor could facilitate chemical combination
may be seen from the following example. Suppose we have
a mixture of hydrogen and chlorine molecules, and that by
some external cause we split up these molecules into atoms ;
half of the hydrogen atoms produced by the dissociation of the
hydrogen molecules will be positively electrified, while the
other half will be negatively electrified ; the same will also be
true of the chlorine atoms. This condition will be permanent
if the negative hydrogen atoms have no opportunities of inter-
changing their charges with the positive chlorine atoms,
and a positive hydrogen atom would thus not be limited to
combining with a negative chlorine one to form a molecule of
hydrochloric acid, but might instead combine with a negative
hydrogen atom to form a hydrogen molecule. If, however,
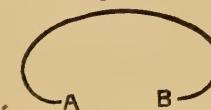
conducting circuits, able to connect atom with atom, were present, the circumstances would be much more favourable to the formation of hydrochloric acid.   For if the conducting circuit stretched from a positive hydrogen atom to a negative chlorine one, these atoms would retain their charges; whereas when the circuits stretched from a negatively electrified hydrogen atom to a positively electrified chlorine one, the atoms would interchange their charges.   Thus the effect of these conducting circuits would be to cause all the hydrogen atoms to be positively electrified, and all the chlorine ones negatively ; this would of course increase the tendency for the hydrogen and chlorine to combine.

In the preceding case we have supposed the molecules to be already split up into atoms ; when, however, we consider the case of a mixture of molecules not already decomposed, we see that something more than the stretching of a conductor from one atom to another is required to effect the interchange of their charges.   For suppose H, H, Cl, Cl (fig. 4) represent

Fig. 4.

$$H \text{———} H$$
$$+ \qquad\quad -$$

$$Cl \text{———} Cl$$
$$+ \qquad\quad -$$
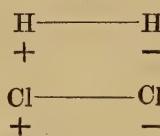
respectively a hydrogen and a chlorine molecule, and suppose that the negative hydrogen atom is connected with the positive chlorine one by a conducting circuit.   Then, if the negative charge of the hydrogen and the positive one of the chlorine were interchanged, the diminution in the potential energy due to the Volta effect would be $2(\sigma_{Cl} - \sigma_{H})$, where σ_{Cl}, σ_{H} are the Volta coefficients of chlorine and hydrogen respectively, σ_{H} being negative.   To set off against this diminution in the potential energy due to the Volta effect, we have the increase in the energy produced by tearing the $-$ charge on the H atom from its proximity to the $+$ charge, and forcing it close to the $-$ charge on the Cl atom.   The increase in the potential energy due to this cause will be of the order $2(V_1 + V_2)$, where V_1 and V_2 are the potential differences between the atoms in the hydrogen and chlorine molecules respectively.   Thus the diminution in the potential energy when the charges are interchanged is

$$2(\sigma_{Cl} - \sigma_{H}) - 2(V_1 - V_2),$$

and the interchange will not go on unless this quantity is positive.   Now the potential difference due to the contact of two substances is equal to the difference of their Volta

coefficients, so that the σ's will not exceed a small number of volts. To estimate the V's is more difficult, but we may remark that when we produce a spark through a gas, in which case there is strong evidence that we split up some of the molecules into atoms, then, no matter how short the spark may be, or what may be the pressure of the gas, the potential difference between the electrodes must exceed a certain value which is very large compared with the potential differences developed by the contact of heterogeneous substances, amounting in the case of hydrogen to between 190 and 200 volts. This minimum potential difference required to produce a spark is so constant under very varying physical conditions, such as pressure, spark-length, and so on, as to suggest that it represents some property of the molecule; and I am inclined to think, and some experiments recently made at the Cavendish laboratory seem strongly to support the view, that the potential difference between the atoms in a molecule placed so as to be free from the action of other molecules is of the order of the minimum potential difference required to produce a spark. In the few cases where a direct estimate has been made of the work required to split up the molecule into atoms, such as that made by E. Wiedemann of the work required to decompose the hydrogen molecule, and that by Boltzmann for the iodine molecule, the potential difference indicated by these estimates far exceeds that produced by the contact of heterogeneous substances.

It would thus appear that in the case of gases where the molecules are free, the condition

$$2(\sigma_{Cl} - \sigma_{H}) > V_1 + V_2$$

is not fulfilled; so that, on the electrical theory, chemical combination would not proceed. To produce chemical combination in such cases there must be some means of lowering the potential difference between the atoms in the molecules. Two methods by which this might take place at once suggest themselves. The first of these is that the combination, instead of taking place between a single pair of molecules, really takes place between aggregates of the molecules, physical aggregation preceding chemical combination.

Thus suppose that a number of molecules form themselves into a chain, such as that represented in fig. 5; then, if we consider a $-H$ atom and the adjacent $+Cl$ one, we see that the disposition of the charges on the atoms of the other molecules in the chain will diminish the work required to separate the $-$ charge on the H atom from the $+$ charge on the

neighbouring H atom, and also that required to separate the
+ charge on the Cl atom from the − charge on the atom
with which it is paired. Thus this disposition of molecules,
by diminishing the electrostatic attractions, increases the
chance for the − H and + Cl to interchange their charges in

Fig. 5.

$$
\begin{array}{c}
\text{Cl} \quad \text{H} \quad \text{H} \quad \text{Cl} \quad \text{Cl} \quad \text{H} \\
\text{Cl} \quad - \quad + \quad - \quad + \quad - \quad + \quad \text{H} \\
+ \\
\text{H} \quad + \quad - \quad + \quad - \quad + \quad - \quad +\, \text{Cl} \\
\text{H} \quad \text{Cl} \quad \text{Cl} \quad \text{H} \quad \text{H} \quad \text{Cl}
\end{array}
$$

(*a*)

$$
\begin{array}{c}
\text{Cl} \quad \text{H} \quad \text{H} \quad \text{Cl} \quad \text{Cl} \quad \text{H} \\
+ \quad + \quad - \quad - \quad + \\
\text{Cl}- \quad\quad\quad\quad\quad\quad\quad\quad +\text{H} \\
\text{H}+ \quad\quad\quad\quad\quad\quad\quad\quad -\text{Cl} \\
+ \quad - \quad - \quad + \quad + \quad - \\
\text{H} \quad \text{Cl} \quad \text{Cl} \quad \text{H} \quad \text{H} \quad \text{Cl}
\end{array}
$$

(*b*)
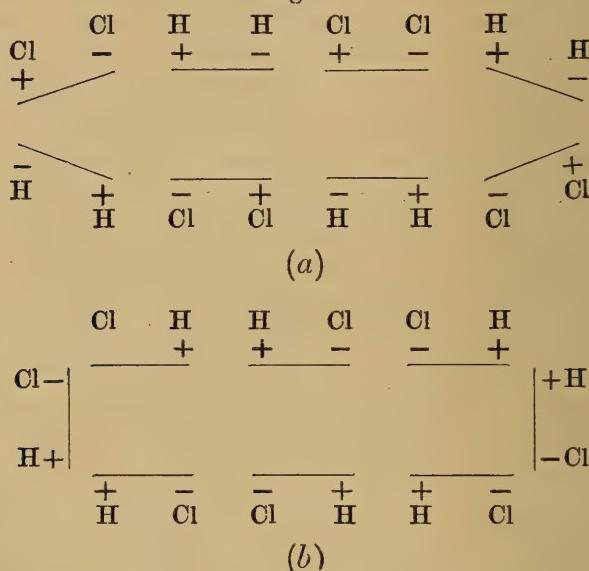
response to the " Volta effect : " after this interchange has
taken place the adjacent H and Cl atoms will have respectively
+ and − charges, *i. e.* charges suitable for the formation of
the HCl molecule ; if such molecules form, the ring will be
disposed as in fig. 5, *b*. This disposition will not be stable,
since the lines joining the negative to the positive atoms in
the molecule do not all point in one way ; the ring will
consequently break up into separate HCl molecules.

Thus, on this view the chemical combination consists in the
formation of an aggregate of a large number of H and Cl
molecules, then the interchange of the charges on some of the
atoms, then the formation of an aggregate of HCl molecules,
and finally the breaking up of this aggregate into a number
of separate molecules of HCl. It will be noticed that there
are no atoms set " free " during the whole of the process.
The presence of free charged atoms during the progress of
chemical combination between gases could be detected by ex-
periments made on the electric conductivity of the mixture
whilst the combination is proceeding. If free charged atoms
are present they will move under electromotive forces, and
will cause the mixture of gases to act as a conductor of elec-
tricity. A method of testing the conductivity of gases and
the results of experiments made with it are given in a paper

by the author (Proc. Camb. Phil. Soc. vol. viii. p. 258). These experiments showed that when a mixture of H and Cl was combining it did not possess any conductivity, thus proving that in these cases no charged atoms were set free during the combination. Some other cases of chemical combination gave the same result; on the other hand there were a class of cases in which the mixture of gases acted as a conductor whilst chemical combination was going on. The experiments thus proved that in many cases of chemical combination no charged atoms are set free.

I also investigated this point by another method. Let us assume for a moment that free charged atoms are liberated during chemical action. To fix our ideas, let us take the case of a piece of zinc attacked by chlorine; suppose now that we electrify the zinc: if chemical action liberated free ions, or, supposing that an aggregation of atoms is necessary, if the algebraical sum of the charges on the atoms forming this aggregate were not zero, then when the electrified zinc atom enters into chemical combination an atom of chlorine must be set free carrying a charge of electricity of the same sign as that on the electrified zinc atom. Thus, in this case the charge would leak from the metal into the gas and the latter would cease to insulate. If, on the other hand, chemical combination went on between an aggregate of atoms the algebraical sum of whose charges was zero, then, however much the zinc was attacked, there would be no liberation of charged atoms and no transference of electricity from the metal to the gas.

I made an extensive series of experiments to find out whether an electrified metal plate when immersed in a gas by which it was chemically attacked did or did not lose its charge. I was never able to trace any leakage of electricity to this cause, even though two metal plates charged to a great difference of potential, either by a Wimshurst machine or by a battery of 2000 small storage-cells, were placed close together in the gas. The electrified surfaces were zinc, mercury, and electrolytic solutions, the gases chlorine and nitrosyl chloride; but though the conditions of the surfaces showed that active chemical action had taken place, there was no escape of electricity through the gas whether the surfaces were positively or negatively electrified. In these cases the chemical combination went on at the temperature of the room when there was no chance of the gas being dissociated. In the case of combination at very high temperatures, when the gas may be dissociated, we shall see later that there are cases where chemical combination does promote the discharge of electricity.

The aggregation of molecules, as described in the preceding sections, is one method by which the attractions between the oppositely electrified atoms in the molecule might be weakened sufficiently to allow chemical action to proceed. Another method by which the same end might be accomplished would be for the molecules to be immersed in, or to be close to the surface of, a conductor or substance of large specific inductive capacity. The effect of this, as explained in the Philosophical Magazine, vol. xxxvi. p. 320, would be to diminish the attraction between the atoms and allow them to be easily separated. The substance which acts as the bridge for the interchange of the charges on the atoms might be the substance which when collected into lumps served by its electrostatic action to diminish the attraction between the atoms. This method of producing chemical change closely resembles the preceding—in each of them the presence of a third substance is necessary, and in each of them the formation of molecular aggregates, but whereas on the first view the aggregates are those of the substances which are combining chemically, on the second they are formed by the third substance.

The hypotheses to which we are led by the preceding considerations may be summed up as follows :—

The forces between charged atoms placed very near together are modified by the electrochemical properties of the atoms. In consequence of this an electronegative atom if positively charged cannot, in the absence of a strong external electric field, interchange its charge with the negative charge on an electropositive atom unless the two are connected by an external conducting circuit.

Chemical action does not (in general) take place between a single pair of molecules alone in the field, but requires the formation of aggregates either of the interacting molecules or of some third substance which is either a conductor of electricity or has a large specific inductive capacity.

In the preceding statement an element is called electropositive or electronegative according as its Volta coefficient is negative or positive.

Thus, on these hypotheses, chemical combination between two elements involves in general two processes :—(1) a process by which all the electropositive atoms, half of which were originally positively and half negatively charged, all become positively charged, while the electronegative atoms become all negatively charged ; (2) the combination of these properly charged atoms to form a molecule of the compound.

In some cases the process of chemical combination seems

only to reach the first stage, that of the interchange of charges between the atoms of the elements. If the process stops at this stage, the electropositive substance will be charged with positive electricity, the electronegative substance with negative electricity. If one of the substances, say the electropositive, is a solid or a liquid, while the other is a gas, then at the surface of the solid or liquid there will be two layers, one of positive electricity on the solid or liquid, the other of negative in the gas. This double layer of electrification will make the electric potential discontinuous at the surface separating the two substances, the potential in the solid just inside the surface of separation exceeding that in the gas just outside the surface by a finite amount. The electrification produced by the splashing of drops is evidence of the existence of this double layer of electrification : when a drop of water or of mercury falls through air and splashes on a plate, the drop itself is positively electrified, while there is negative electrification in the surrounding air. On the view just given, this is an example of incomplete chemical combination: in the case of the water, the electrical interchanges preliminary to the formation of H_2O_2, the oxygen in the air getting the negative charge, have taken place ; the second stage, however, does not go on, or at any rate is not completed during the falling of the drop. Thus the positively and negatively electrified atoms are not bound together so firmly as they are in a chemical compound, and get separated in the great extension of surface produced by the splashing. In the case of mercury the first stage of oxidation, that is the assumption of the negative charge by the oxygen and of the positive by the mercury, occurs, while the second either does not occur or is not completed during the fall of the drop. It would seem from the phenomena of drops that examples of this incomplete chemical action are very frequent, for the splashing of drops of the most widely different substances gives rise to electrification. In fact it seems possible that the existence of this double coat, and on our hypothesis of incomplete chemical action, is almost universal at ordinary temperatures, and that the electrification produced by the friction of heterogeneous substances is due to the partial rubbing off of this coating from one or both of the substances.

We shall now proceed to consider in the light of this hypothesis as to chemical action several simple chemical and electrical phenomena. We shall begin with the case of oxidation. Let us suppose that we have a zinc rod immersed in oxygen, and in order to take a case where the chances of combination are greatest, let us suppose that the oxygen molecules are dissociated by some external agent into atoms.

Suppose that the combination begins, ZnO being formed.
Since a positive charge is withdrawn from $\overset{+}{\text{the}}$ $\overset{-}{}$ zinc and a
negative one from the oxygen, the zinc and oxygen, which
were originally electrically neutral, will now be charged nega-
tively and positively, so that at the surface of contact of the
zinc and the oxygen a charged condenser will be formed with
its negative charge carried by the zinc atoms, its positive
charge by the oxygen atoms. According to our hypothesis,
zinc and oxygen atoms in these electric states do not combine
unless connected by conducting circuits, so that, unless such
circuits are present, for each molecule of ZnO formed there
will be an increase in the charge on the condenser, and con-
sequently an increase in its potential energy. The charge on
the condenser is proportional to the number of molecules of
ZnO formed, so that the electrostatic potential energy will be
proportional to the square of the number of molecules; the
diminution in the chemical potential energy due to the
formation of ZnO is only proportional to the number of
molecules of this substance. Thus the increase of the potential
energy increases faster with the number of molecules of ZnO
formed than the diminution in the energy; so that after a
certain amount of chemical combination has occurred, any
further combination will be attended by an increase in the
total potential energy. When this point has been reached
chemical combination will stop; so that under these circum-
stances only a limited amount of chemical combination will
occur. Suppose now, however, that in addition to the zinc
and oxygen other substances are present which can form con-
ducting circuits between the negative zinc and the positive
oxygen atoms, and thus enable these atoms to interchange
their charges, so that the zinc becomes positively, the oxygen
negatively electrified. In this state they can combine so that
the condenser at the surface of the zinc will be discharged.
As this condenser is constantly being discharged, there will be
no increase in the potential energy due to it, and thus the
progress of the chemical action will be accompanied by a
diminution in the potential energy, and will therefore proceed
until one or other of the substances is exhausted.

Similar considerations will show why but little chemical
action goes on if zinc is immersed in acid, while the action
proceeds freely when the zinc is connected to the acid by an
external conducting circuit.

It is easy to find an expression for the difference of
potential reached between the plates of the condenser formed
at the surface of the zinc when there is no external con-

ducting circuit. Let us take the case of zinc immersed in acid, suppose we have a rod of zinc immersed in a solution of zinc chloride. We may suppose that in the solution we have positively charged zinc atoms, negatively charged chlorine ones, and molecules of zinc chloride, consiting of a positive zinc atom combined with a negative chlorine one. When a stick of zinc is immersed in the solution, some of its positively charged zinc atoms combine with the negative chlorine ones in the solution and form neutral zinc chloride. This leaves on the zinc rod an excess of negative electricity, while in the solution there will be an excess of positive electricity carried by the zinc atoms. These atoms approach the rod and form one plate of a condenser, the other plate of which consists of the negatively electrified zinc atoms in the rod, the charge in this condenser will be proportional to the number of molecules of zinc chloride formed.

We can find the potential difference between the plates of this condenser when equilibrium is reached in the following way :—When equilibrium is reached the mean Lagrangian function of the system will be stationary.

Now the Lagrangian function consists (1) of a part due to the solvent; as this does not change during the process of chemical combination we may leave it out of account. (2) A part due to the zinc rod ; this will be of the form $m_1 Z_1$ where m_1 is the mass of the zinc in the rod, and Z_1 a quantity independent of m_1. (3) A part due to the zinc chloride in solution; if m_2 is the mass of $ZnCl_2$, then this part of the mean Lagrangian function is equal to

$$-m_2 R_2 \theta \log m_2 + m_2 w_2$$

(see 'Applications of Dynamics to Physics and Chemistry,' p. 154) : here θ represents the absolute temperature, w_2 a quantity independent of m_2, while $R_2 \theta$ is equal to the pressure exerted by a number of molecules of $ZnCl_2$ in the gaseous state and obeying Boyle's law divided by the density of the gas in this state. (4) A part due to the zinc atoms in the solution; if m_3 is the mass of these atoms, this part of the Lagrangian function is equal to

$$-m_3 R_3 \theta \log m_3 + m_3 w_3.$$

(5) A part due to the Cl atoms in the solution; if m_4 is the mass of these atoms, this part is equal to

$$-m_4 R_4 \theta \log m_4 + m_4 w_4.$$

(6) A part due to the condenser formed at the junction of the zinc and the solution ; if C is the capacity of this condenser

and Q the charge, this part of the Lagrangian function will be equal to

$$-\frac{1}{2}\frac{Q^2}{C}.$$

Thus the total variable part of the Lagrangian function, which we shall denote by H, is given by the equation

$$H = m_1 Z_1 - \theta(m_2 R_2 \log m_2 + m_3 R_3 \log m_3 + m_4 R_4 \log m_4)$$

$$+ (m_2 w_2 + m_3 w_3 + m_4 w_4) - \frac{1}{2}\frac{Q^2}{C}.$$

When things are in a steady state the value of this function is stationary, hence

$$\frac{dH}{dm_1}\delta m_1 + \frac{dH}{dm_2}\delta m_2 + \frac{dH}{dm_3}\delta m_3 + \frac{dH}{dm_4}\delta m_4 + \frac{dH}{dQ}\delta Q = 0, \quad . \; (1)$$

for all consistent values of δm_1, δm_2, δm_3, dm_4, δQ.

One possible change in the system is for n atoms of zinc in the rod to combine with $2n$ atoms of Cl to form n molecules of $ZnCl_2$. Q will, if we take as unit charge the charge carried by a monad atom, be increased by $2n$, since zinc is a dyad. Hence

$$\delta m_1 = -n, \; \delta m_2 = +n, \; \delta m_3 = 0, \; \delta m_4 = -2n, \; \delta Q = 2n;$$

so that by (1) we have

$$-\frac{dH}{dm_1} + \frac{dH}{dm_3} - \frac{2dH}{dm_4} + \frac{2dH}{dQ} = 0.$$

Since $\dfrac{dH}{dQ} = -\dfrac{Q}{C} = -V$, where V is the potential difference between the plates of the condenser, we have

$$V = \frac{1}{2}\left\{ \frac{dH}{dm_2} - \frac{dH}{dm_1} - \frac{2dH}{dm_4} \right\}. \quad . \; . \; . \; (2)$$

Another change that could take place in the system is for n of the atoms of zinc in the solution to combine with $2n$ of the chlorine atoms to produce n molecules of $ZnCl_2$. In this case

$$\delta m_1 = 0, \; \delta m_2 = n, \; \delta m_3 = -n, \; \delta m_4 = -2n, \; \delta Q = 0.$$

Thus equation (1) becomes

$$\frac{dH}{dm_2} - \frac{dH}{dm_3} - \frac{2dH}{dm_4} = 0; \quad . \; . \; . \; . \; . \; (3)$$

hence from (3) and (4) we have

$$V = \frac{1}{2} \left\{ \frac{d\mathrm{H}}{dm_3} - \frac{d\mathrm{H}}{dm_1} \right\} . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

Now $d\mathrm{H}/dm_3$ depends solely upon the number of zinc atoms in unit volume of the solution, while $d\mathrm{H}/dm_1$ is independent of the solution altogether. Hence we see that the potential difference between the zinc and the solution depends solely upon the number of free zinc atoms in unit volume of the solution. If this be constant the potential difference is the same whatever salt of zinc is used.

From the value found for H we see

$$V = \tfrac{1}{2} \{ - \mathrm{R}_3 \theta \log m_3 + \text{a term independent of } m_3 \}, \quad . \quad (5)$$

thus

$$\frac{d\mathrm{V}}{dm_3} = - \frac{1}{2} \frac{\mathrm{R}_3 \theta}{m_3} .$$

An expression which shows how the potential difference varies with the strength of the solution.

We see from equation (5) that the magnitude and even the sign of V depends upon the value of m_3, the number of free zinc ions in the solution. If m_3 is less than a certain quantity V is positive, that is the positive coating of the double layer formed at the zinc surface is in the electrolyte, while the negative is on the zinc; when m_3 exceeds this value, the signs of the coatings are reversed. For infinitely dilute solutions the value of V would be infinite. Though equation (5) enables us to find the value of V when m_3 is known, the equations are insufficient to determine this quantity in such a case, for example, as when a zinc rod is immersed in a solution of HCl: here $ZnCl_2$ may be formed by chemical action and dissolve in the zinc, and then partly be split up into Zn and Cl atoms. In this case we have in the solution molecules of $ZnCl_2$ and HCl, atoms of Zn, H, and Cl. Let m_5 denote the number of atoms of H, m_6 the number of molecules of HCl, the rest of the notation being the same as before. Then to determine the variables we have the equations 2, 3, 4, and since one way in which the system could vary would be by an atom of hydrogen combining with an atom of chlorine to form a molecule of hydrochloric acid, we have

$$\frac{d\mathrm{H}}{dm_6} - \frac{d\mathrm{H}}{dm_5} - \frac{d\mathrm{H}}{dm_4} = 0. \quad . \quad . \quad . \quad . \quad . \quad (6)$$

Since the total number of hydrogen and chlorine atoms contained in the solution must be equal to N, if N is the number of hydrochloric acid molecules originally taken for the

solution, we have

$$m_5 + m_6 = N, \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (7)$$

$$m_4 + 2m_2 + m_6 = N. \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (8)$$

Thus to determine the 6 quantities $m_2 \ldots m_6$, V, we have only the five equations (3), (4), (6), (7), (8). The charge on the condenser $Q = 2m_2$, and $V = Q/C$; hence if we know C the capacity of the condenser we have another equation connecting the six quantities, so that they can be determined. To calculate C, however, we should require to know the distance between the plates of the condenser, that is the distance between the positively and negatively charged zinc atoms. We do not know this distance, but if we had a series of measurements of V we should by the preceding equations be able to calculate m_2, and hence the capacity of the condenser, and from this capacity the distance between the two layers.

The preceding expression gives the potential difference between the zinc and the electrolyte on the supposition that these are not connected by an external conducting circuit; the presence of such a circuit might, however, so modify the conditions as to render the preceding considerations quite inapplicable. Thus, take the preceding case of zinc immersed in dilute HCl, if the solution is exceedingly dilute, we have on the surface of the zinc a number of positive hydrogen atoms. If the Volta effect could come into play there would be a diminution in the potential energy of the whole system, if the $-$ zinc and the $+$ H interchanged their charges: in the absence of the external circuit this on our hypothesis is impossible, but it would take place if such a circuit were present. In this case the negative charges on the zinc atoms would be replaced by positive, the potential of the zinc instead of being lower than that of the electrolyte would be higher. This illustrates the principle that the two causes which tend to produce potential differences between substances in contact, viz. direct chemical combination and the interchange of charges on the atoms, tend to establish potential differences of opposite sign. Chemical combination tends to make the electropositive substance negative to the electronegative one, since the positive atoms combine while the negative ones are left, while the interchange of charges tends to make the electropositive substance positive to the electronegative. Thus, when two substances are placed in contact under varying physical conditions, the sign of the potential difference will depend upon the relative intensity of these two effects. Observation seems to prove that a difference in

the sign of the contact potential difference between two sub-
stances does take place when the circumstances are altered in
such a way that we might expect great changes in the relative
importance of these effects to occur. Thus there are cases
where, when the substances are cold, when we should expect
the chemical action to be sluggish, the electropositive sub-
stance is at a higher potential than the electronegative one,
while when the temperature is that of red heat or higher,
when chemical action is presumably more vigorous, the sign
of the potential difference is reversed. Thus, for example,
when a drop breaks off from a column of mercury and falls
through oxygen, the mercury is positively, the oxygen nega-
tively electrified : again, when ultra-violet light falls upon
a clean metal plate, the metal is positively, the surround-
ing air negatively electrified. In this case the sign of
the potential difference indicates that the effect due to the
interchange of charges overpowers that due to the chemical
combination. If, however, we have a piece of metal above a
red heat surrounded by air, the air will acquire a positive
charge, the metal a negative one ; so that in this case the effect
of chemical combination overpowers any effect that may be
due to the interchange of atoms.

The contact of the zinc with the solution in the preceding
example thus gives rise to the formation of two layers of
atoms, one layer being positively, the other layer negatively
electrified. When the solution is very weak, this double layer
which is interposed between the zinc and the solution consists
of a layer of partly dissociated zinc molecules, the positive
atoms being next the solution, the negative atoms next the
zinc plate. If the solution is strong, the transition between
the zinc and the solution is made by a layer of partly dissociated
molecules of the salt, the positive layer, consisting of zinc
atoms, being next the zinc, the negative layer, consisting of
atoms of the electronegative constituent of the salt, being
next the solution. In the case of the contact of a metal and
the electrolyte, the work required to produce the double
electrical layer which gives rise to the potential difference is
in the preceding investigation supposed to be done by the
osmotic pressure. There is, however, another source of energy
quite adequate to produce potential differences at the surfaces
of contact of different substances, and which is available in
the case of solids as well as liquids. This source is surface-
tension. Every unit of area of the surface of separation of
two substances, A and B, contributes an amount of potential
energy equal to the surface-tension between A and B. Now
Lord Rayleigh has shown (Phil. Mag. October 1883, p. 315)

that, if the transition from A to B, instead of being abrupt, takes place through a thin layer (whose thickness need only be commensurable with molecular distance) whose properties are intermediate between A and B, the potential energy due to surface-tension will be diminished. This diminution in the potential energy will produce a tendency for such a transitional layer to be formed, even though the formation of the layer is accompanied by a double layer of electrification. The energy rendered available by a sensible diminution in the surface-tension will be more than sufficient to charge the double layer of electrification up to a potential difference amounting to a large fraction of a volt. For if the distance between the electrified layers is 10^{-8} centim., and their potential difference 1 volt, the energy per unit area of the condenser formed by the double layer will be equal to $10^{16}/8\pi \times 10^{-8} \times 9 \times 10^{20}$, or about 44 ergs. If the surface-tension were the same as that of water, the energy due to it would be 78 ergs per square centimetre, so that if any sensible diminution in this took place, the energy rendered available would suffice to charge up the layer to a potential difference comparable with a volt. Even if the formation of this layer required as a preliminary chemical decomposition to liberate the charged atoms forming the layer, and this decomposition required a supply of energy, there would still be plenty available for this purpose. The thickness of the layer is comparable with the range of molecular forces; thus the quantity of matter in it, and therefore the amount of chemical decomposition, will be exceedingly small, so small as to be quite imperceptible by chemical means, but small as it is it may, in consequence of the enormous electric charges carried by the atoms, be sufficient to produce a finite potential difference between the coats of the double layer.

The amount of energy which would be liberated by a diminution in the abruptness of transition, and the effects which this might be expected to produce, are, I think, much greater than is generally suspected. Thus we should, for instance, expect that the abruptness of transition between, say, a metal like mercury and a gas like oxygen, would be diminished if between the mercury and the gas there was a film of the compound of the two: the tendency to form this compound would be very great, for if the film of oxide only diminished the surface-tension by one per cent., enough energy would be liberated to suffice to raise the temperature of a film of oxygen 10^{-8} centim. thick several hundred degrees Centigrade. With this amount of energy available, it is difficult to avoid the conclusion that even the least oxidizable metals must, when exposed to air, be coated with a thin film of oxide, and though

this film is too thin to be detected, either by chemical or optical means, it may yet, as we have seen, produce appreciable electrical effects. The same effects, too, might be expected to take place between solids : thus, if copper and zinc were brought into intimate contact, there would be a tendency for a layer of brass to form between them, it does not seem impossible that under favourable circumstances the zinc and copper might be cemented together by this film of brass.

This consideration, too, must have an important application to the electrification due to the splashing of drops; this phenomenon requires the existence of a double coating of electricity over the surface of the drop, to provide the atoms which carry the charges on these coatings chemical decomposition may have to take place. The energy for this may come from the lowering of the surface-tension produced by the formation of an intermediate layer, so that at the surface of the drop chemical changes may take place, of which we have at ordinary temperatures no experience from experiments made with large masses of the substances.

Contact-difference of Potential between a Metal and a Coating of Oxide.

If we have a metal plate covered with a film of oxide or other compound of the metal, the transition from the metal to the air will be more gradual if the molecules of the compound in the part of the film near the plate are arranged so that the metal atoms are next the plate, and the oxygen atoms on the far side. In the molecules of the oxide, the metal atoms carry the charge of positive electricity, while the oxygen atoms carry the negative charge : there will thus at the surface of the plate be a double coating of electricity, the positive side of this layer being next the plate, the potential, therefore, will fall as we pass from the metal to the layer of oxide, that is the oxide will be negative to the metal. This agrees with the results obtained by those who have experimented on contact-electricity, and it further appears, as a possible interpretation of their experiments, that the potential difference between a metal and its oxide may amount to a considerable fraction of a volt.

Communication of Electricity from the Electrified Atoms of a Gas to a Conductor.

This is only another aspect of the preceding question. For suppose we have a number of electrified atoms of a gas in contact with a metal, and that the metal is electropositive to the gas, the electricity can go from the gas to the metal in the following ways :—(1) If the atoms of the

gas are negatively electrified, they may combine with positive atoms of the metal to form a neutral compound, leaving an excess of the atoms of the metal negatively electrified. Or, if the atoms of the gas are positively electrified, then, if any substance is present which can form conducting chains between the atoms of the gas and those of the metal, the atoms will interchange their charges, the positive charge going to the electropositive substance and the negative to the electro-negative. Those atoms of the gas which were positively charged might unite with those negatively charged to form molecules, so that the gas itself would emerge electrically neutral after contact with the metal.

It will be seen that each of these methods requires something more than mere contact of the gas and metal, this seems borne out by the phenomena exhibited by electrified gases. It was shown by Giese that electrified gases from a flame could pass through wire gauze connected with the earth, and yet retain their charges : this fact is exemplified in a very striking way by Lord Kelvin's electric strainers, as he finds that electrified gases still retain an appreciable fraction of their charges after passing through these strainers which consist of many layers of wire gauze placed one behind the other. In an experiment I described in the B. A. Report for 1894 ("The Connexion between Chemical Combination and the Discharge of Electricity through Gases"), an electrified gas retained its charge though enclosed in a vessel with a large pool of mercury connected to the earth. I have also found that such gases retain a large proportion of their charge after bubbling through a mixture of sulphuric acid and water. In a paper "On the Passage of Electricity through Hot Gases" (Phil. Mag. [5] xxix. p. 444), I showed that when a current is flowing through a hot gas a piece of cold metal interposed between the electrodes completely stops the current, though when the metal gets red hot the current passes through it with ease. In all these cases the charged atoms would be striking against conductors, so that they furnish very strong evidence that this process alone is not sufficient to rob the atoms of their charges.

The first of the processes alluded to above would tend to make a gas lose a negative charge or the metal a positive one, while the second process would make the gas lose a positive charge, the metal a negative one. This is on the assumption that the metal is electropositive to the gas; if it were electro-negative, the words positive and negative must be interchanged in the preceding statement.

The first process involves chemical combination, thus anything tending to promote combination, such as a high tem-

perature of the gas or metal, would increase this effect ; we should therefore expect to find evidence of this effect in the case of hot bodies.   A very good instance of this effect is the fact, discovered by Guthrie, that a hot ball of iron could retain a negative charge when it could not retain a positive one.   The experiments of Elster and Geitel also illustrate this point.   Again I found (see Proc. Roy. Inst. April 13, 1894), that if in a vessel containing hydrogen (and probably a little air) at a low pressure, we split up some of the molecules of the gas so as to get a supply of positively and negatively electrified atoms, a red-hot clean copper rod connected with the earth would discharge the negative electricity and leave the positive behind.   The negative electricity escapes from the gas, since the negatively electrified gaseous atoms combine chemically with the positive atoms of the metal. If, however, a red-hot copper rod thickly coated with oxide is placed in the gas, the *positive* electricity escapes from the gas through the rod to the earth.   This is in accordance with the theory ; the chemical process which now goes on is the reduction of the oxide : and this is effected by the positive hydrogen atoms combining with the negative oxygen atoms, thus the process affords a means of escape to the positive electricity in the gas, but not to the negative.

The second process by which we have explained the escape of electricity from a gas is that of the interchange of charges between oppositely charged atoms.   As the tendency for this process to take place arises from the Volta effect, it will be great when we have a number of strongly electropositive atoms charged with negative electricity near a number of electronegative ones charged with positive electricity.   Thus we should expect the effect to be great when one of the substances is an electropositive metal, as when this is in an electrically neutral state half the strongly electropositive atoms are charged with negative electricity, and on account of the Volta effect there is a great tendency for them to lose their charges.   When, however, we have an electrolyte instead of the metal, we should expect the effect to be much smaller, as in an electrolyte the electropositive element has the positive charge, the electronegative one the negative ; it might, however, still exist to some extent if, for example, the electrified gas in contact with the electrolyte were more electronegative than the negative element of the electrolyte, and if the gas carried a positive charge.

This difference between metals and electrolytes may perhaps be the explanation of the fact that, whereas a sheet of metal when illuminated by ultra-violet light rapidly loses a negative charge while it can retain a positive one, this effect being

most pronounced the more electropositive the metal, an electrolyte, on the other hand, when exposed to ultra-violet light does not lose its charge, whether this be positive or negative.

Another example of the discharge of electricity by the second process, is that in the glow-discharge from a metal where the temperature is low the negative discharge occurs more easily than the positive, *i. e.* the potential difference between the point from which the electricity escapes and the nearest large conductor is less when the point is negatively electrified than when it is positively. It would be interesting to see whether this difference would still persist if the point from which the discharge takes place were made of an electrolyte and not of metal. On the hypothesis we have just been describing, we should expect the difference to be much reduced by the substitution of an electrolyte for the metal. Some recent experiments by Prof. S. P. Thompson show that the conditions of discharge are modified when lead peroxide is substituted for metal.

When a glow-discharge takes place from a metal point connected directly with a Ruhmkorff coil or a Wimshurst electrical machine the surrounding gas gets negatively electrified. This, however, is not always the case if we connect the point from which the discharge takes place to an instrument producing potential differences greatly exceeding those given by a Ruhmkorff coil. A very convenient form of such an instrument is the one described by Prof. Elihu Thompson, which is a transformer whose primary is a coil connecting the outside coatings of two Leyden jars, while the secondary is a coil with a large number of turns carefully insulated from the primary. When the oscillating current produced by discharging the jars passes through the primary, the electromotive force induced in the secondary is able to induce sparks of great length. Using a transformer of this kind instead of the Ruhmkorff coil, Harvey and Hird (Phil. Mag. vol. xxxvi. p. 45) and Himstedt (Wied. *Ann.* lii. p. 473) found that when the point discharged in oxygen, the gas was *positively* electrified, while when it discharged in hydrogen, the hydrogen was negatively electrified, just as when the Ruhmkorff is used. The very intense field produced by the transformer would split up the molecules of the gas and promote direct combination between the metal and the gas ; this, as we have seen, would cause the gas to be positively, the metal negatively electrified, and this, as we have seen, is what happens in the case of oxygen, though not in that of hydrogen. In the case of the electrification of the

air in a vessel into which a point is discharging, we have to consider not only the communication of electricity from the point to the gas, but also the diffusion of the electrified atoms of the gas from the neighbourhood of the point through the vessel. Any difference in the rate of diffusion would, even though the communications of $+$ and $-$ electricity from the point to the jar were made with equal ease, give rise to an electrification of the gas. Imagine, for example, that negatively electrified atoms diffuse through the gas more quickly than positively electrified ones; then, if the rates of emission of $+$ and $-$ electricity were the same, the negatively electrified atoms would get further from the point than the positive, so that the outlying regions would get a charge of negative electricity ; the region round the point would be charged with positive electricity, part of this would leak back into the point, leaving the gas as a whole negatively charged. Several phenomena, which I shall now proceed to describe, have led me to the conclusion that the effects due to the communication of the electricity from the metal to the gas are masked in many cases by the difference in the rates at which the electrified atoms diffuse, the negative atoms in all my experiments diffusing more rapidly than the positive ones. In the case of oxygen, where the gas gets a positive charge, the strong tendency for the oxygen to combine with the metal is sufficient to overcome the more rapid diffusion, whereas with such gases as hydrogen and carbonic acid, where the tendency to combine is weaker, diffusion gets the upper hand.

I made several experiments with chlorine, using different materials for the discharging point. The first substance I tried was silver chloride which had been fused into a solid mass; when this point was connected to one of the terminals of the high tension transformer, the chlorine was negatively electrified. I then used a zinc point, protecting the zinc before the experiment began by covering it with a glass tube, through which it was pushed just before the discharge began ; in this case, again, the chlorine was negatively electrified to a slight extent. I then replaced the zinc point by a sodium one, protecting this in the same way as the zinc by a glass tube ; when the discharge passed from the sodium point, the chlorine was *positively* electrified. Thus by using a substance such as sodium, which has a very great affinity for chlorine, we are able to overcome the effect of diffusion, and get a positive charge in the gas, just as when the discharge passes from a copper point into oxygen.

The following experiments seem to show that a negatively

electrified hydrogen or oxygen atom moves more quickly under equal electric intensities than a positively electrified one.

The outside coatings of two Leyden jars, A, B (fig. 6), were connected by a wire wound into a coil C. In this coil an exhausted bulb was placed and a platinum wire fused into the bulb ; this wire was connected with an electrometer. The inside coatings of the jar were connected with the terminals of an induction-coil through the primary of which the alternating current used for lighting the laboratory passed. This caused an arc-discharge to pass between the terminals of the induction-coil, and produced a potential difference between the insides of the jars. This potential difference can be very greatly increased by directing a blast of air on the space between the terminals of the induction-coil, and so blowing out the arc.

Fig. 6.

If we now examine the electrical state of the platinum wire in the bulb, we shall find that, when the blast is on, the wire acquires a positive charge when placed near the equator of the bulb (by the equator of the bulb we mean the region inside the bulb adjacent to the coil which encircles it), and a negative charge when placed near the pole. If, however, after the blast has been on for some time, it is suddenly stopped and the arc allowed to pass between the terminals of the induction-coil, the sign of the electrification is reversed, the platinum wire now acquiring a positive charge when placed at the pole of the bulb and a negative charge when placed at the equator. Both these results are, I think, explicable if we suppose that the negative atoms diffuse more rapidly than the positive ones. For, take the case when the arc is blown out. Here there is a great potential difference between the electrodes, and the coil surrounding the bulb is raised to a high potential. This causes a brush-discharge to start from the glass into the rarefied gas in the bulb, the discharge starting from the part of the glass nearest the coil, *i. e.* from the equator. If, now, the negative atoms travel faster through the bulb than the positive, then, even though the same number of the two kinds of atoms start from the glass, the negative atoms will be in excess in the region remote from the origin of the discharge, while near this origin the positive atoms will be in excess : thus we shall have positive electrification at the equator, negative electrification at the poles. Let this go on until a number of positive and negative atoms are dispersed through the bulb. Then stop the blast. This at once
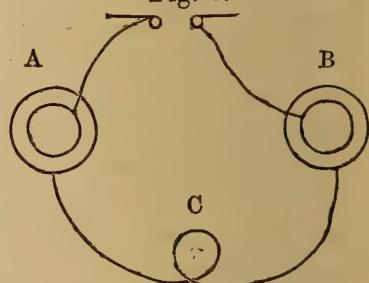
greatly diminishes the potential difference between the terminals of the induction-coil, and lowers the potential of the coil surrounding the bulb to such an extent that the brush discharge no longer takes place from the glass : the electric intensity in the bulb is lowered, so that no further decomposition of the gas takes place, and the bulb now does not show any luminosity.   The charged atoms produced by the previous discharge linger for some time in the bulb before recombining, and move under the electric intensity due to the oscillating currents in the coil ; the lines of electric intensity arising from the induction due to these currents are circles, with the line joining the poles of the bulb for their axis.   Under these forces the atoms will tend to describe these circles ; and since the negative ones move more quickly than the positive ones, the negative atoms will be revolving round the axis of the bulb with greater rapidity than the positive ones : hence, on account of centrifugal force, there will be an excess of negative atoms at the equator, and consequently an excess of positive ones at the pole : thus the equator will be negatively, the poles positively electrified.   This electrification is, however, only transient, as the opposite charged atoms soon recombine.

If the negative atoms move more quickly than the positive ones, then in a discharge-tube in a steady state the pressure at the positive electrode must be higher than that at the negative.   For at any part of such a tube where there is no excess of positive electrification, the number of negative atoms which in unit time cross a section of the tube is greater than the number of positive ones.   There will thus be a stream of *atoms* towards the positive electrode : to keep the pressure in the tube constant, we must compensate this by a stream of *molecules* from the positive to the negative electrode.

To calculate this pressure, let us suppose that the discharge-tube is cylindrical of radius a.   Let i be the current through the tube, u the velocity of the negative ions, v the velocity of the positive ; then in unit time the number of atoms lost by the side of the tube next the negative electrode and gained by the side of the tube next the positive is equal to

$$\frac{i}{\epsilon}\frac{u-v}{u+v},$$

where ϵ is the charge carried by one of the atoms.

To keep the pressure constant, the positive side of the tube must lose, and the negative side gain this number of molecules.   If P is the pressure-gradient, μ the coefficient of

viscosity, ρ the density of the gas, and m the mass of a molecule, then the number of molecules which in unit time cross a section of the tube is

$$\frac{\rho}{m}\frac{P\pi a^4}{8\mu}.$$

Hence we have, when the pressure is steady,

$$\frac{\rho}{m}\frac{P\pi a^4}{8\mu}=\frac{u-v}{u+v}\frac{i}{\epsilon},$$

or

$$\frac{P\pi a^4}{8\mu}=\frac{1}{\rho}\frac{u-v}{u+v}\cdot\frac{im}{\epsilon}.$$

Thus the potential gradient will vary inversely as the pressure of the gas, and the ratio of the pressure at the positive electrode to that at the negative will depend upon the square of the reciprocal of the pressure.

Taking the case of a tube 1 millim. in diameter, 10 centim. in length, filled with hydrogen at a pressure of one ten-thousandth of an atmosphere, and conveying a current of one ten-thousandth of an ampere, I find from the preceding formula that, supposing u much greater than v, the pressure at the positive electrode would exceed that at the negative by about twenty per cent.

XLIX. *Proceedings of Learned Societies.*

GEOLOGICAL SOCIETY.

June 19th, 1895.—Dr. Henry Woodward, F.R.S., President, in the Chair.

[Continued from p. 395.]

THE following communications were read:—
3. 'The Chalky Clay of the Fenland and its Borders : its Constitution, Origin, Distribution, and Age.' By Sir Henry H. Howorth, K.C.I.E., M.P., F.R.S., F.G.S.

The distribution of the Clay (so often termed Chalky *Boulder* Clay) is noticed, and it is stated that it is surrounded on all sides by country occupied by different deposits, being mainly separated from the sea on the east and north-east by sandy and pebbly materials, while on every other side it is clearly and sharply defined. The paucity of foreign stones is noted as compared with natives, and the similarity of the matrix of the Chalky Clay to the material of the older deposits of the neighbourhood. The author maintains that the contents of the Clay indicate movement of material from west to east

in some places, as shown by Jurassic fossils in the East Anglian Chalky Clay, and from east to west in others : in fact, that movement took place in sporadic lines diverging from the Wash and the Fens. He appeals to the amount of disintegration that has taken place to furnish the material for the Clay, the shape of the stones in the Clay, and the distribution of the Clay itself, as evidence against the action of land-ice or icebergs, maintaining that there is no evidence of submergence at the time the Clay was formed ; and criticizes the attempts made to explain the formation of the Clay by water produced by the melting of ice.

The author believes that the denudation of the Fen country which produced the great mass of the Chalky Clay with most of its boulders was coincident with and caused by the bending and folding of the Chalk of Eastern England, which took place after the deposition of the Crag beds, and that during the period of folding a great depression was formed round the Wash, into which the water rushed from the North carrying débris and mixing it with clays ; this, rushing into what was virtually a *cul-de-sac*, dispersed and scattered its load in all directions.

4. ' On the Occurrence of *Spirorbis*-Limestone and thin Coals in the so-called Permian Rocks of Wyre Forest ; with Considerations as to the Systematic Position of the " Permians " of Salopian Type.' By T. Crosbee Cantrill, Esq., B.Sc.Lond.

In South Staffordshire a thick series of red rocks—the so-called Lower Permian—overlies the ordinary yellow and grey Coal Measures, and underlies the Triassic rocks. They consist of sandstones, marls, calcareous conglomerates, and breccias, having a general red or purplish-red colour.

Since Jukes's work was published, fresh sinkings have shown that these red rocks must be regarded as of Upper Coal Measure age, because their included fossils have an Upper Coal Measure *facies*. The rocks contain bands of limestone characterized by the presence of *Spirorbis pusillus* : those parts of the series which have not yielded Coal Measure fossils are apparently similar lithologically to those which have yielded them ; there is no stratigraphical break between the fossiliferous and unfossiliferous parts of the red series, and the only marked breaks are at the base and summit of the series, the break at the base being locally great but elsewhere practically imperceptible.

The evidence furnished by the deposits of the Forest of Wyre (= Enville) district also leads the author to regard the red rocks associated with *Spirorbis*-limestone and coals as Upper Coal Measures, exhibiting a gradual passing away of Coal Measure conditions and the in-coming of those of New Red Sandstone times ; and these passage-beds must be regarded as much nearer the Coal Measure than the Permo-Triassic end of the transitional period.

So far as our present knowledge goes, the so-called Permian rocks of Anglesey, Denbighshire, Lebotwood, Shrewsbury, Coalbrookdale,

Wyre Forest, South Staffordshire, Warwickshire, Leicestershire, and North Staffordshire are all essentially similar ; and observers are urged to look out for coal-seams, plant-remains, and *Spirorbis*-limestones.

November 6th.—Dr. Henry Woodward, F.R.S., President,
in the Chair.

The following communications were read :—

1. 'The Serpentine, Gneissoid, and Hornblendic Rocks of the Lizard District.' By T. G. Bonney, D.Sc., LL.D., F.R.S., F.G.S., Professor of Geology and Mineralogy in University College, London.

After some introductory remarks the author states that in company with the Rev. E. Hill, and in consequence of their work in Sark, he again investigated the question of the genesis of the hornblende-schists at the Lizard, and was able to overcome the difficulties which formerly withheld him from attributing an igneous origin to the schists themselves and their banded structures to fluxional movements during consolidation. Here also, as in Sark, there is some evidence of this banding being the result, at any rate in places, of a mixture of a less and a more basic material. Additional evidence is given as to the genesis of the granulitic group and its relations to the hornblende-schist. Moreover, in consequence of the paper by Messrs. Fox and Teall, published in the Society's Journal (vol. xlix. p. 199), the author has again examined (with Mr. Hill) every section which he could discover to bear on the relations of the serpentine, the hornblende-schist, and the granulitic rock. A number of instances are quoted, where the serpentine splits open or rumples the bands of the granulitic rock, or cuts across them. He shows that in the sections at Potstone Point and elsewhere the serpentine is welded to the hornblende-schist, cuts across its banding, and behaves generally as an intrusive rock, while the rare cases of apparent interstratification of the two prove to be the results of the inclusion and occasional very local melting down of the latter by the former rock. He maintains that the relations of the serpentine to the granulitic and the hornblendic groups are inexplicable on the hypothesis of an igneous complex, so far as he understands the meaning of that term, or of a folding in a solid condition or any other form of dynamometamorphism, and he maintains his original opinion that the serpentine (*i. e.* the original peridotite) is intrusive in the other rocks.

The paper also deals with some minor points in the geology of the Lizard ; the author supplying some additional particulars about the serpentine at Porthkerris and Porthallow, and explaining that he has found the rocks on the south side of Porthoustock Cove to be only a continuation of those which form the crags south of the opening of the Cove, though they are generally less well preserved : namely, a fine-grained gabbro, intrusive in the ordinary Crousa Down gabbro, and 'greenstone' dykes cutting both of these.

2. 'The "Schistes Lustrés" of Mont Jovet (Savoy).' By J. W. Gregory, D.Sc., F.G.S.

The author gives a history of the controversy as to the age of the 'schistes lustrés' of the Western Alps, making special reference to the views of Zaccagna and Bertrand concerning the schists of Mont Jovet. Of these writers, the former maintains that the rocks of the summit of the mountain are old rocks on which the Carboniferous and Triassic strata were deposited unconformably; while, according to the latter author, the rocks forming the top of the mountain were laid down after those which flank it.

In the present paper the author gives the results of an examination of the rocks of Mont Jovet recently made by him. He contends that Lory and Zaccagna were correct in identifying the central rocks of Mont Jovet as 'schistes lustrés,' for this conclusion is supported by their lithological characters and the occurrence of basic igneous rocks of the 'pietre-verdi' type associated with them, and is not opposed to their stratigraphical relations. It is further maintained, as the result of the evidence collected by the author, that the schists in question are older than the Trias; for fragments of the schists occur in the Trias, there is a discordance of strike between the two series, masses of dolomite rest unconformably upon the flanks of the schists, and the Trias has escaped metamorphism which the schists have undergone. The probabilities are in favour of the schists occupying the same relation to the Carboniferous as they do to the Trias; while the close approximation of the schists to the former shows that the schists are not the altered representatives of the neighbouring Carboniferous beds, and it is therefore concluded that the 'schistes lustrés' are pre-Carboniferous, but evidence by which finally to assign them to any exact horizon before this date is still wanting.

L. *Intelligence and Miscellaneous Articles.*

ON THE WAVE-LENGTH OF THE D_3 HELIUM LINE.
BY A. DEFOREST PALMER, JR.

OWING to the recent increased interest in the wave-length of the helium lines due to the discovery of terrestrial helium, I have been led to calculate some observations on the D_3 chromosphere line carried out by myself at the Physical Laboratory of the Johns Hopkins University during February and March 1893.

The measurements were made on the large fixed telescope-spectrometer, used by Dr. Louis Bell[*] in his determination of the absolute wave-length of the D solar lines, with a plane speculum metal grating having about fourteen thousand lines to the inch and 5 inches of grating-space. The telescopes of this instrument are 16·4 centim. clear aperture and about 2·5 metres focal length; and with the grating used I obtained good dispersion and excellent definition in the first spectrum to the right of the normal to the

[*] Amer. Journ. Sci. vol. xxxv. p. 265; Phil. Mag. 1888, xxv. p. 245.

grating. All the observations were made in this spectrum on account of its superior definition.

An image of the sun about 1 centim. in diameter was formed on the slit of the instrument by aid of a large Foucault heliostat, and an achromatic lens of about four inches aperture. Appliances were provided for moving the image laterally across the slit, and, by means of a total reflecting prism, for turning it about the direction of the beam as an axis to bring any desired point of the limb over the slit.

The D_3 line appeared only when the sun's image was tangent to the slit, and then as a bright but very short line in the centre of the field of view vertically considered. Its definition and intensity were found to vary greatly from day to day, and for different points on the sun's limb. In general, when a solar prominence lay across the slit the line was very broad and intense; but the definition of its edges was poor, thus rendering it impossible to set the cross-hairs on it with accuracy. The best combination of intensity and definition was obtained by avoiding prominences and working only on very clear days.

The observations were made by the ordinary micrometric method, the D_3 line being compared with the best solar standard lines in the field of view. The wave-lengths of these standard lines, as taken from Prof. Rowland's "Table of Standard Wave-lengths"†, were :—

Fe	5916·475	Fe	5862·580
Fe	5914·384	Fe	5859·810
Fe	5905·895	Ba	5853·903
Na.D_1	5896·164	Average value.	5887·028

Seventeen series of measurements were made, in each of which equal numbers of observations were taken on diametrically opposite points of the sun's limb in order to eliminate the effect of rotation.

The wave-length of D_3 was calculated from each of these series by Prof. Rowland's method of interpolation, on the assumption that, for the space used, the spectrum was essentially normal. The average of the seventeen values thus found gives

$$5875 \cdot 939 \pm \cdot 006$$

for the wave-length of the D_3 line, the probable error being calculated from the deviations of the several values from the mean in the usual manner.

To test the accuracy of the observations and method of calculation, the wave-length of the mean line was computed from the observations and found to be 5887·027, a value which differs only by ·001 from the average of the wave-lengths of the standard lines used, 5887·028.

I am indebted to Prof. H. A. Rowland and Dr. J. S. Ames for permission to use apparatus and for suggestions, and to Mr. W. S. Day for aid in making the observations.—*American Journal of Science,* November 1895.

* Astr. and Astro.-Phys. vol. xii. p. 321; and Phil. Mag. [5] xxxvi. p. 49.

INDEX to VOL. XL.

END OF THE FORTIETH VOLUME.

Steel collar screwed in
slate block

C A

screwed gland
Asbestos and
mica washers

copper t

wire pyrometer

SECTION (

e of the bridge

ie bridge slider through the galvanometer

N

threaded ~ 36 threads to the inch

Steel collar screwed in
slate block

A

C

steel collar

Mica Washer

screwed gland
Asbestos and
mica washers

wooden cap

SECTION OF PYROMETER
Fig.1.

Compensating
leads

Main leads

END VIEW.

to the middle of the bridge

C

Q

P

Contact breaker
actuated by
exhaust valve

Indicator
on engine
making contact
on explosion

A
Battery

E

D

Ebonite Distance piece

Crank shaft of engine

to the bridge slider through the galvanometer

R S Mercury cup T

Ebonite block

Electro-
magnet
M

DIAGRAM SHOWING CONNECTIONS FOR CLOSING GALVANOMETER CIRCUIT.
Fig. 3.

Fig. 2.

copper tube

wire pyrometer

wrought iron tube

standard
pyrometer

worm on the same
spindle as pulley

SECTION OF TUBE FURNACE SHOWING PYROMETERS IN POSITION.
Fig. 4.

Key

Resistance Box

Galvanometer

Main leads of pyrometer

Key

Daniel's Cell

8 ohms

8 ohms

Compensating leads of
pyrometer

A

C

D

B

Bridge wire

Slider

DIAGRAM OF BRIDGE CONNECTIONS.
Fig. 2.

S
S
S

S
S
S

S
T
T
Th

Th

Temperature
on Air Scale.

900

1000

1100

1200

Fig. 5.

Line of zero pressure

Mean Indicator Diagram. Jan. 1–4. 1895
Vertical Scale 120 lbs = 1 inch.
Fig. 8.

Temperature
on Air Scale

Fig. 5

Mean Indicator Diagram. Jan 1–4. 1895
Vertical Scale 120 lbs = 1 inch.
Fig. 8.

Line of Zero pressure

——— Jan 4 ·0025 wire — — — Jan 4 ·003 wire — · — · Jan 1 ·003 wire ········ Jan 2 ·0025 wire ·········· Jan 1 ·003 wire

percentage of
stroke.

Fig. 6.

Mean Indicator Diagram Jan 31 Mar 7. 1895.
Vertical Scale 120 lbs = 1 inch.
Fig. 9.

Line of Zero pressure

——— Feb 12 ·0025 wire — — — Feb 12 ·002 wire — · — · Jan 31 ·0025 wire ·········· May 7 ·0025 wire

Temperature
on Air Scale

Fig. 7.

Mean Indicator Diagram. Mar 16 20 1895
Vertical Scale 120 lbs = 1 inch.
Fig. 10.

Line of Zero pressure.

0   10   20   30   40   50   60   70   80

Jan 4 .003 wire = — = Jan 1 .003 wire = — = Jan 2 .0025 wire .... Jan 1 .0

percentage of

0° Cent

h

pt°

P₁

+

B−

Cross Section.

sheet copper

copper tube

mica

Outside view of Thermometer

Section along Axis of Thermometer

G

Ebonite Distance piece

Platinoid leading wires

R SUREMENTS

100 cms. of platinum wire.

1·25″

thin mica

·25″ — ·04″

·35″

·50″

Fig. 1.

PLATINUM THERMOMETER
used for Thermo electric experiments.

ARRANGEMENT OF COMBINED
RESISTANCE BALANCE AND POTENTIOMETER FOR THERMO-ELECTRIC MEASUREMENTS

For Bridge, connect Cups 4 to 5 and 1 to 7.
For Potentiometer, connect Cups 3 to 4 and 6 to 7.
to measure E.M.F. and Cups 2 to 3 and 6 to 7 to
to check by Clark's cell.

Fig. 2
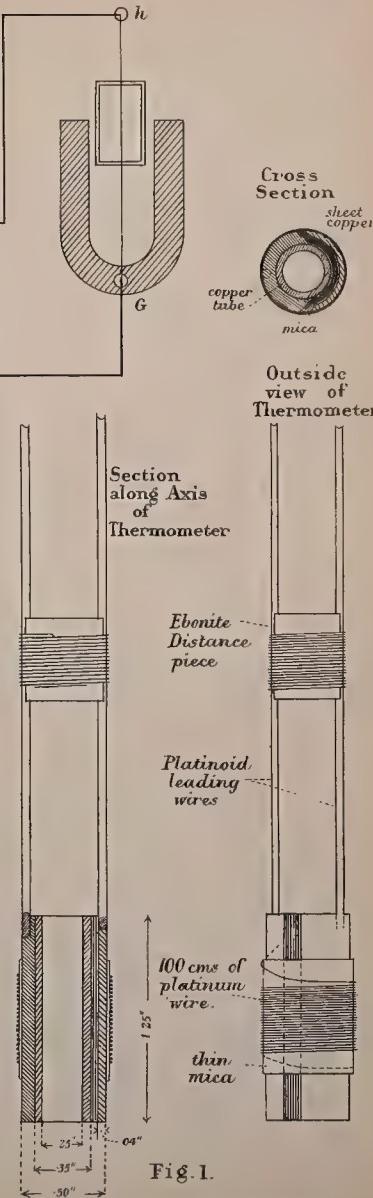
PLATINUM THERMOMETER
used for Thermo electric experiments.

Fig. 1.
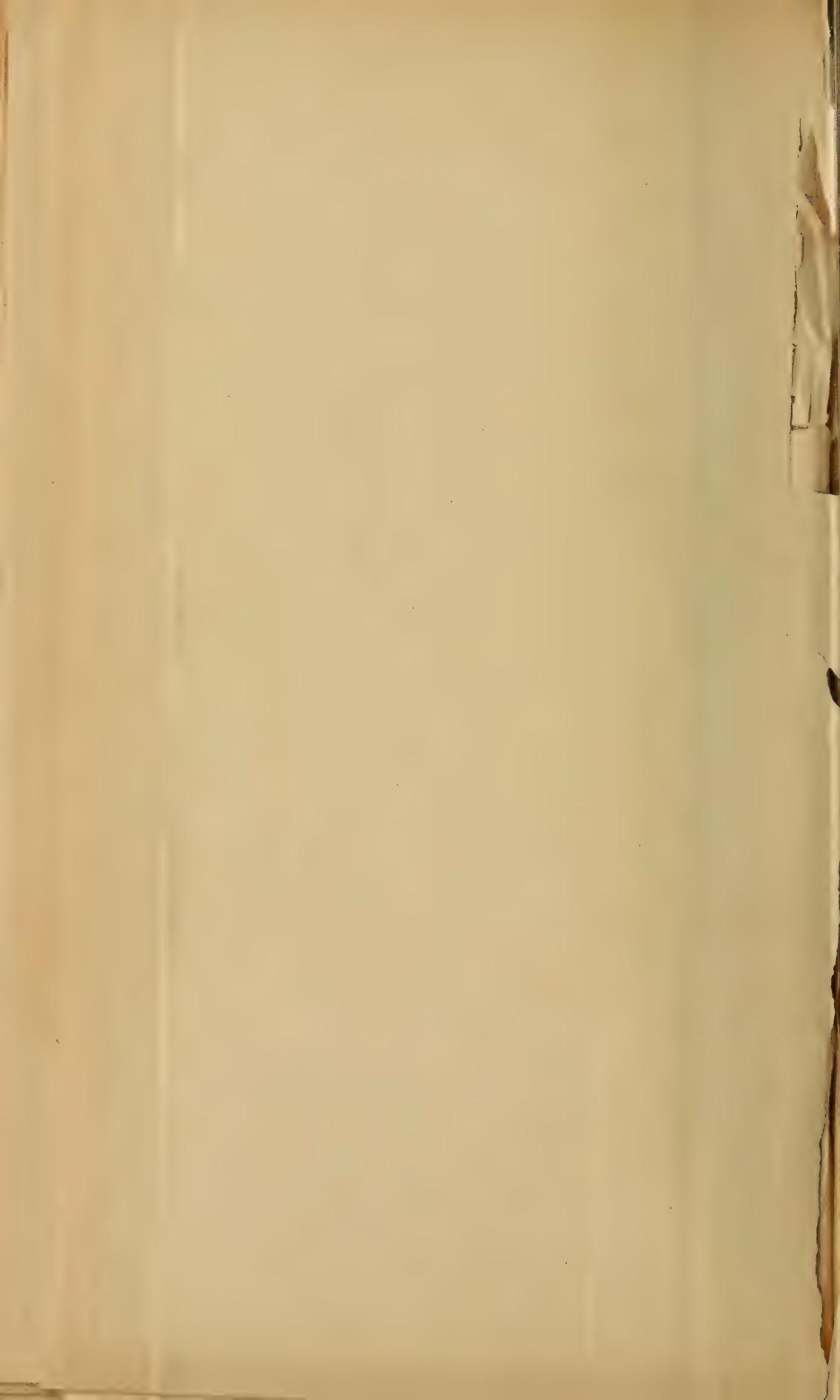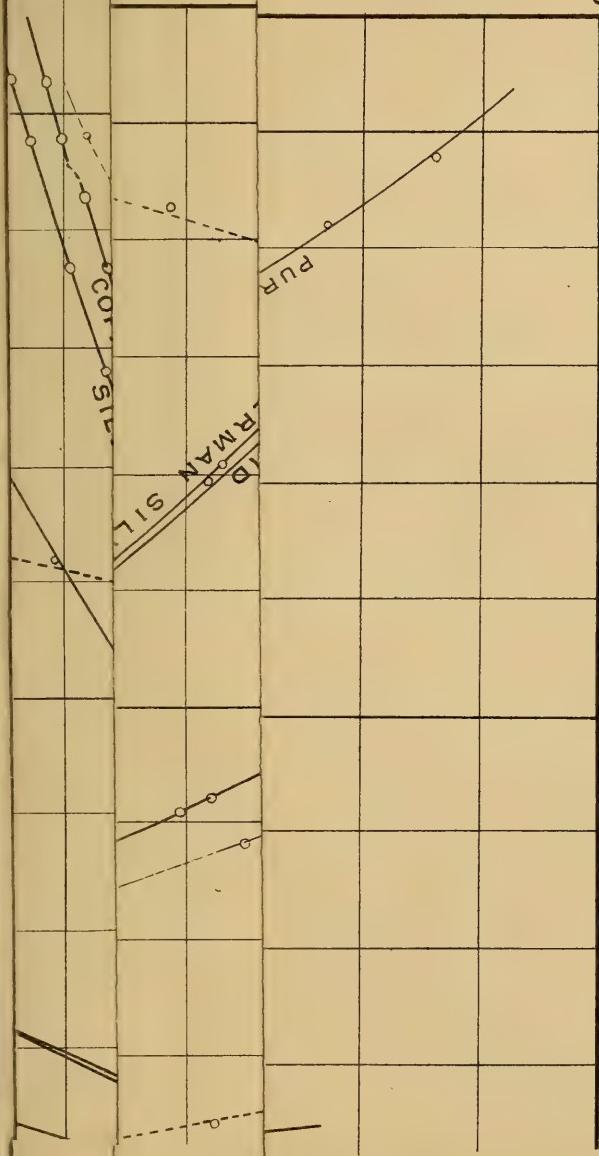
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OF

PURE METALS AND '

DEWAR AND FLEMI!

+250,000

COP SIL

RMAN SIL

PUR

PUR
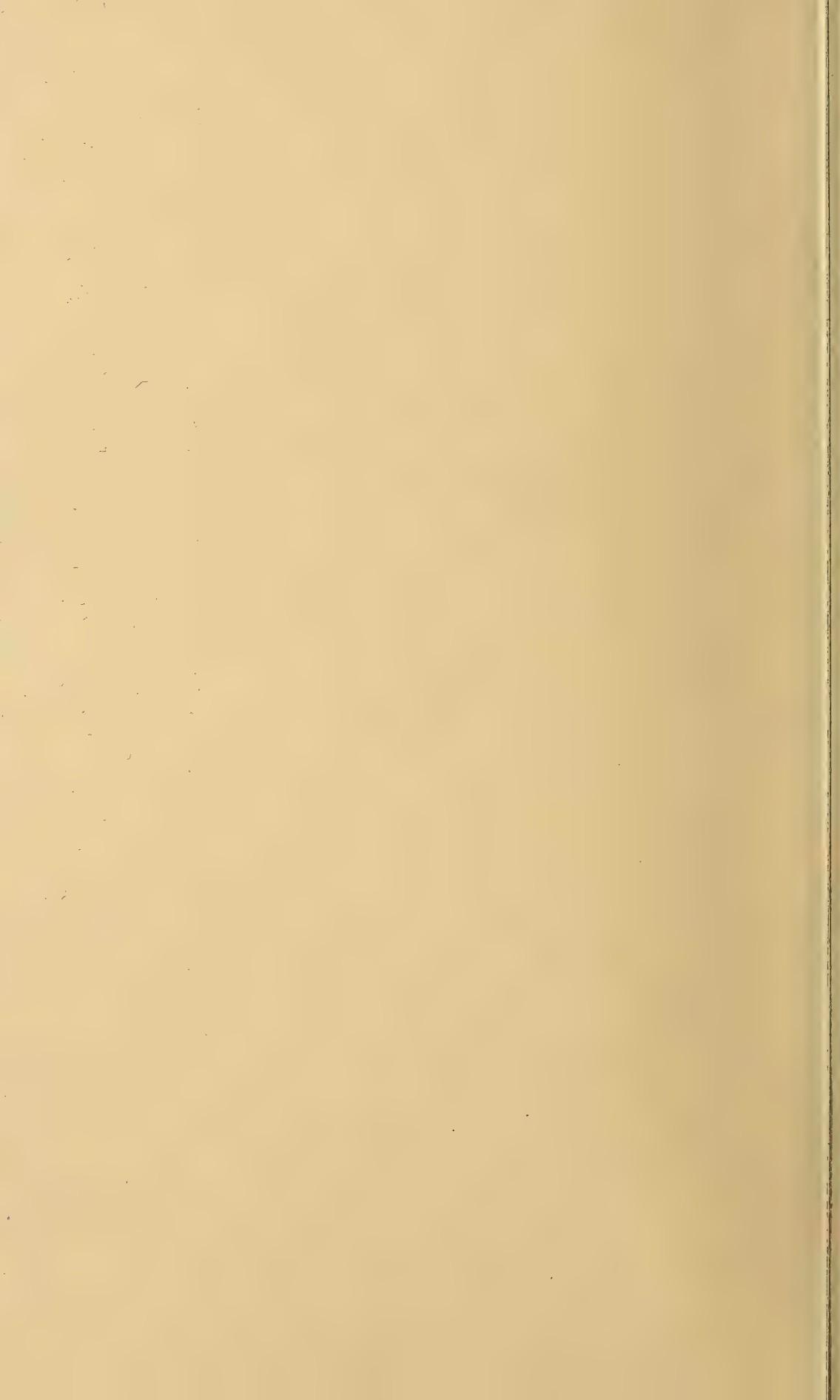
THERMO-ELECTROMOTIVE FORCE
OF
PURE METALS AND ALLOYS.
DEWAR AND FLEMING

ELECTROMOTIVE FORCE IN C.G.S. UNITS.

TEMPERATURE IN PLATINUM DEGREES.
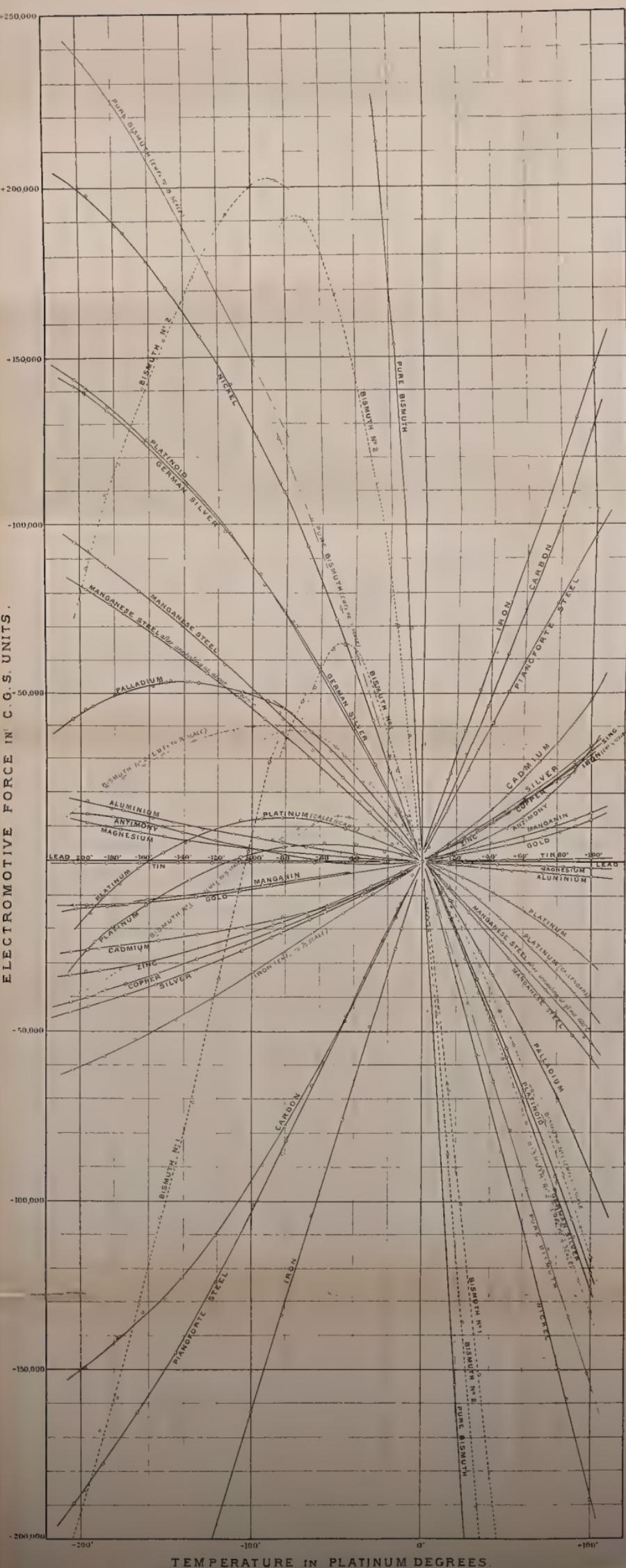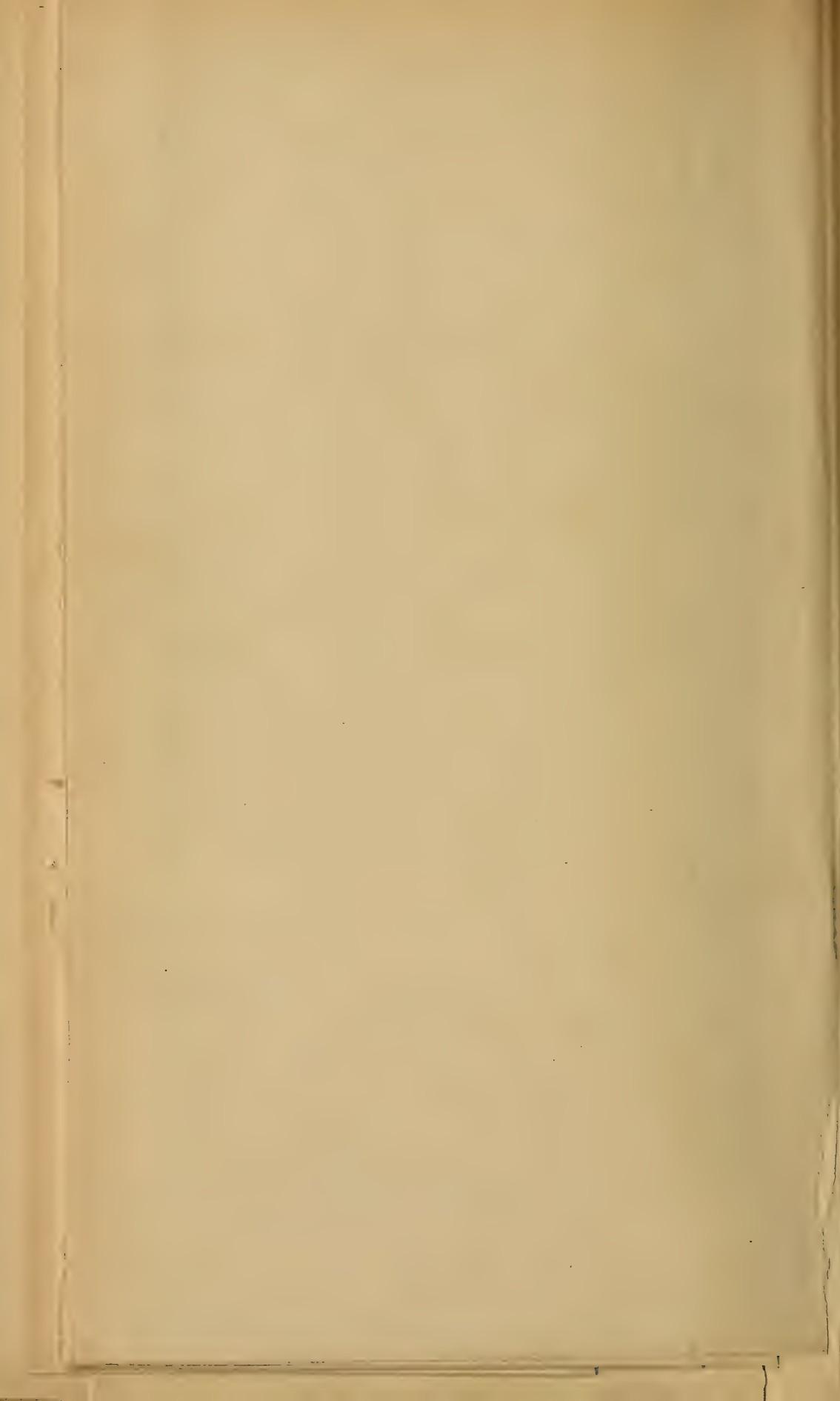
H WITH TEMPERATURE.

SPECIFIC RESISTANCE IN C.G.S. UNITS.

300,000

200,000

100,000

0°   +100°
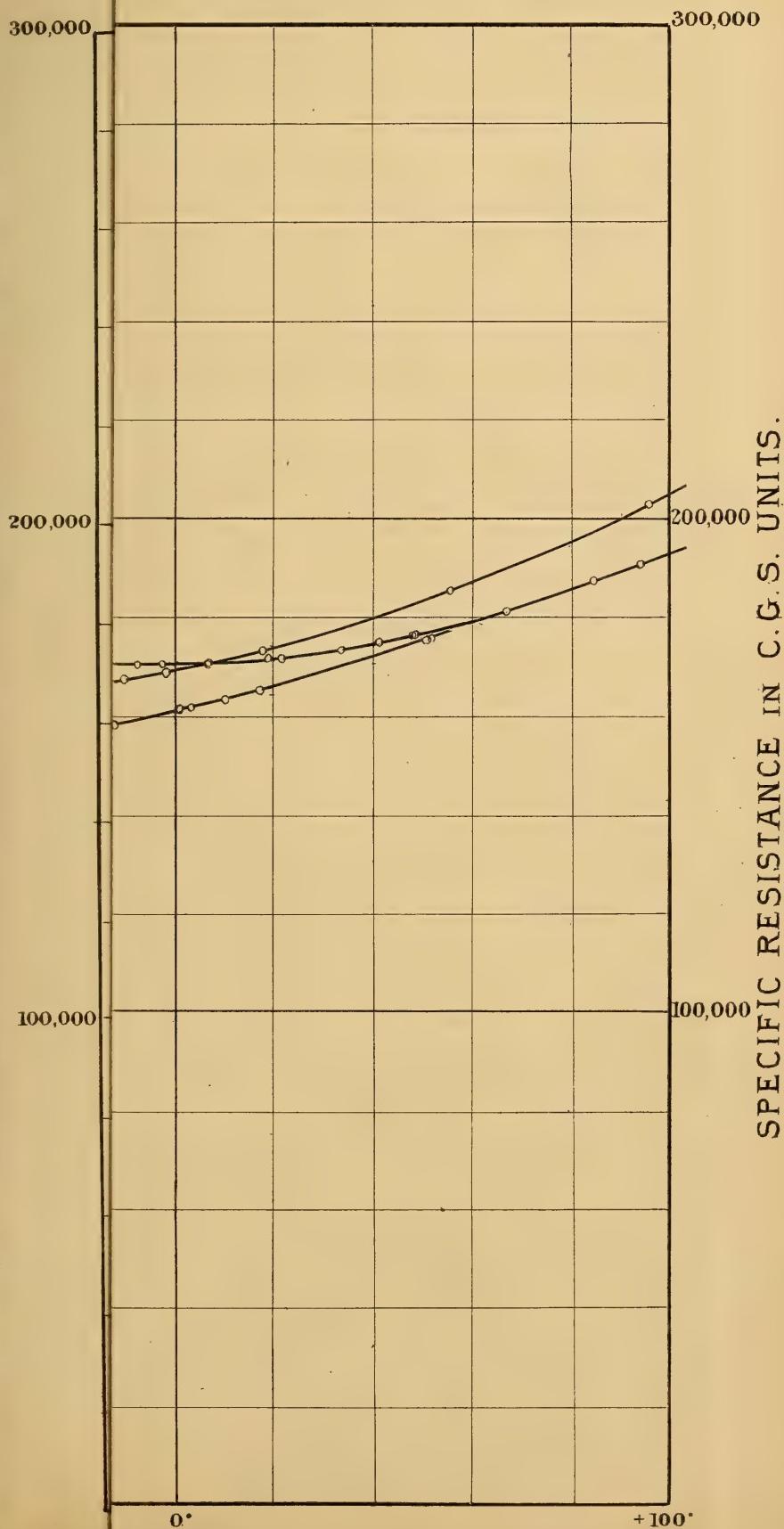
THE VARIATION OF ELECTRICAL RESISTANCE OF BISMUTH WITH TEMPERATURE.

DEWAR AND FLEMING.

SPECIFIC RESISTANCE IN C.G.S. UNITS.

TEMPERATURE IN PLATINUM DEGREES.
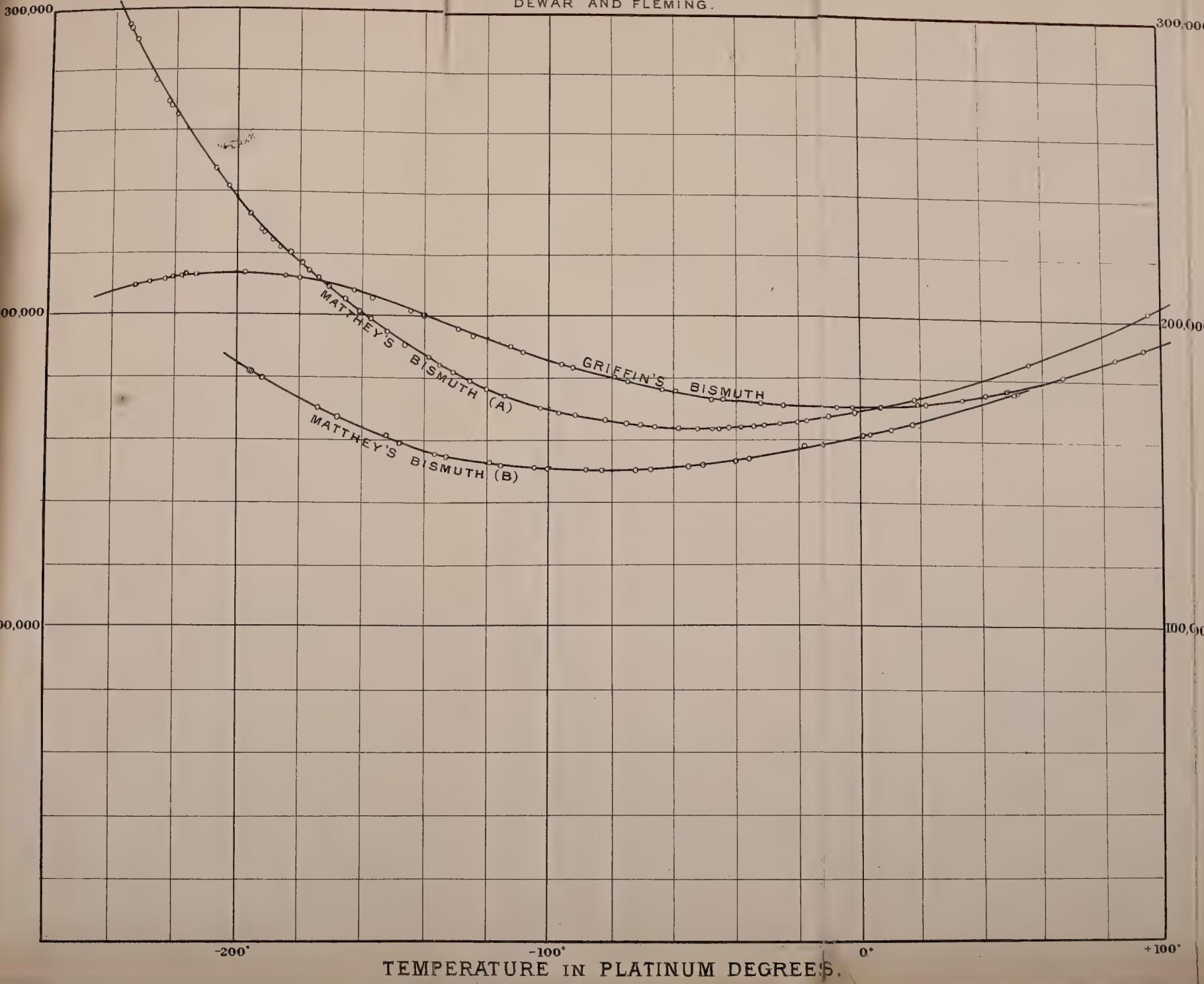
Capacity for Heat of Water from 10° to 30° C. referred to its
Capacity at 15° C. as unity.

1·00193
1·00121

Bartoli & Str. corrected

1·00076
1·00036
1·00004

Regnault

·99944
·99882
·99867
·99858
·99762

·99764
·99744

Griffiths

·99646

Rowland (mixture)

·99570

Rowland (mech.)

1·00262 Rowland (mech.)
1·00207 Mean of R & B & S
B + S.
1·00152
Rowland (mixture)
1·00118
·99969
Regnault

Mean of R, B & S & G.

10°   15°   20°   25°   30°

1·0030
1·0020
1·0010
1·0000
·9990
·9980
·9970
·9960
·9950
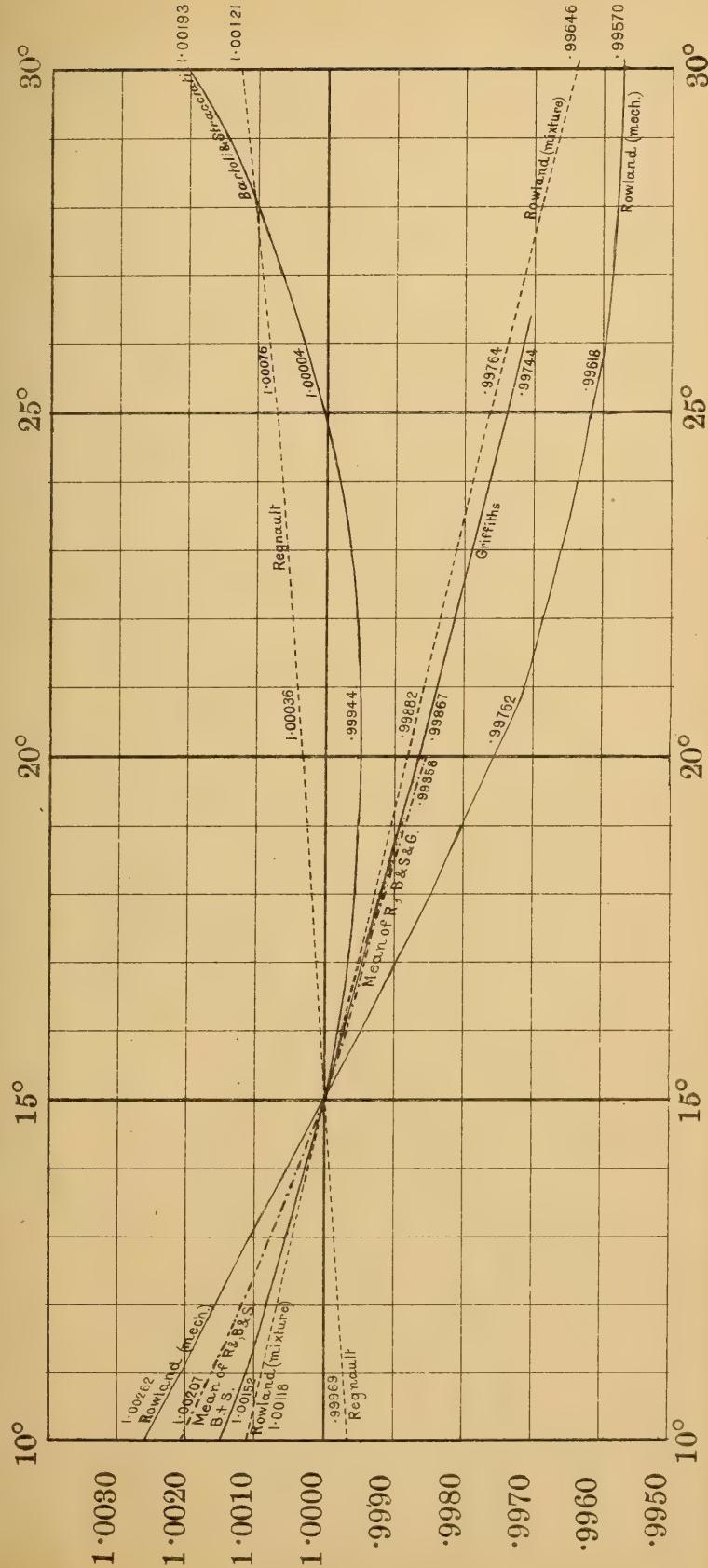
$$\text{Mean} \begin{cases} (15° \text{ to } 20°) \text{ of Rowland, Bart. \& Str., and Griffiths} = 1 - ·000284\,(\theta - 15) \\ (10° \text{ to } 15°) \text{ of Rowland (mech), and Bart. \& Str.} = 1 + ·000414\,(15 - \theta) \end{cases}$$

The Capacity for Heat of Water in terms of the Thermodynamic unit.

42·30 × 10⁶

42·20 ,,

42·10 ,,

42·00 ,,

41·90 ,,

41·80 ,,

41·70 ,,

5°   10°   15°   20°

Rowland

4·212

4·2041
4·2036

Griffiths

4·198

4·1954

4·1924

Shuster & Gannon

4·1991

Griffiths

4·1893
4·1883

4·889

Micalescu

4·1827

Joule (R) *1

4·1820
4·1810

Rowland

4·190

Joule (S) *2

4·174

5°   10°   15°   20°
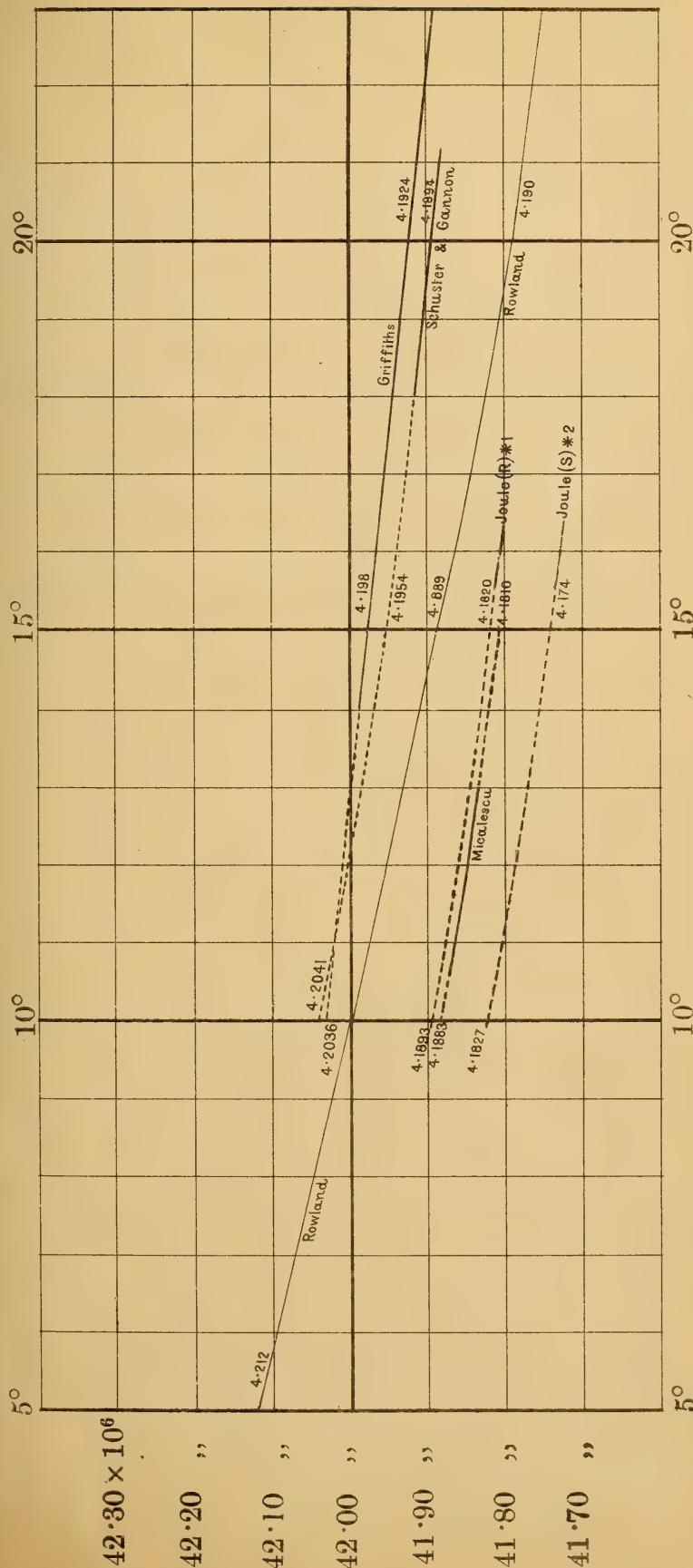
Mean of all observers { Assuming Joule (R) *1 ... at 10° = (41·971 ± ·023) × 10⁶, at 15° = (41·891 ± ·023) × 10⁶

,,   ,,   (S) *2 ....   ,,   = (41·958 ± ·029) × 10⁶,   ,,   = (41·875 ± ·029) × 10⁶

*1 Joule (R) = Joule's later expᵗˢ in terms of Rowland's air thermometer.

*2 Joule (S) =   ,,   ,,   ,,   the nitrogen (International) scale, according to Schuster

Edwin Wilson, Cambridge

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